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INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

THE object of the abstracts of chemical papers published elsewhere in the Transactions of the Society is to furnish the Fellows with a concise account of the progress of chemical science from month to month. It must be understood that as the abstracts are prepared for the information of the Fellows in general, they cannot possibly be so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally.
2. Before beginning to write the abstract, the whole of the original paper must be read, in order that a judgment may be formed of its importance and of the scale on which the abstract should be made.
3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.
4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper.
5. The abstract should be made as short as is consistent with a fair and accurate statement of the author's results.
6. A concise statement showing the general trend of the investigation should be given at the commencement of those abstracts where the nature of the original permits of it.
7. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should, as a rule, be made of this fact.
8. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.
9. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned only shortly. On the other hand, data such as melting and boiling points, *sp. gr.*, specific rotation, &c., must be given in every case unless recorded in earlier papers.

Nomenclature.

10. Employ names such as *sodium chloride*, *potassium sulphate* for inorganic compounds, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chlorides, sulphurous and sulphuric acids.

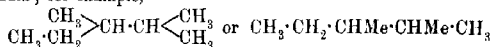
11. Term compounds of metallic radicles with the OH-group *hydroxides* and not hydrates, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation.

12. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as sodium hydrogen sulphate, disodium hydrogen phosphate, &c., to the acid salts. Basic salts as a rule are best designated merely by their *formulae*.

13. Names in common use for oxides should be employed, for example: NO, nitric oxide; CO₂, carbon dioxide; P₄O₁₀, phosphoric oxide; As₂O₃, arsenious oxide; Fe₂O₃, ferric oxide.

14. In open chain compounds, Greek letters must be used to indicate the position of a substituent, the letter *a* being assigned to the first carbon atom in the formula, except in the case of CN and CO₂H, for example, CH₃·CH₂·CH₂·CH₂I *a*-iodobutane, CH₃·CH₂·CH₂·CN *a*-cyanopropane.

15. Isomeric open chain compounds are most conveniently represented as substitution derivatives of the longest carbon chain in the formula; for example,



should be termed *βγ*-dimethylpentane not methylethylisopropylmethane, and $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{array} > \text{CH} \cdot \text{CH} < \begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CO}_2\text{H} \end{array}$ or CH₃·CHMe·CHMe·CO₂H should be termed *αβ*-dimethylbutyric acid, not *αββ*-trimethylpropionic, or *α*-methylisovaleric, or methylisopropylacetic acid.

16. Use names such as methane, ethane, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form CH₃·[CH₂]_n·CH₃, &c. Term the hydrocarbons C₂H₄ and C₂H₂ ethylene and acetylene respectively (not ethene and ethine). Homologues of the ethylene series are to be indicated by the suffix *-ene*, and those of the acetylene series, wherever possible, by *-ine*. Adopt the name *allene* for the hydrocarbon CH₂:C:CH₂.

17. Distinguish all hydroxyl derivatives of hydrocarbons by names ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, or *n*-hydric, according to the number of OH-groups. Compounds which are not alcohols, but for which names ending in *ol* have been used, are to be represented by names ending in *ole*, if a systematic name cannot be given, thus anisole not anisol, indole not indol. Compounds such as MeONa, EtONa, &c., should be termed sodium methoxide, sodium ethoxide, &c.

18. The radicles indicated in the name of a compound are to be

given in the order fluoro-, chloro-, bromo-, iodo-, nitro-, nitroso-, amino-, imino-, cyano-, thiocyno-, hydroxy-, keto-.

19. Compounds analogous to the acids of the lactic series containing the OH-group should be termed *hydroxy-*derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups OEt, OPh, OAc, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus α -ethoxypropionic acid, $\text{OEt}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, instead of ethyl-lactic acid; 3:4-diethoxybenzoic acid, $(\text{OEt})_2\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$, instead of diethylprotocatechuic acid; and α -acetoxypropionic acid, $\text{OAc}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, thus, $\text{C}_6\text{H}_5\text{Et}_2(\text{OH})_2\cdot\text{CO}_2\text{H}$, and not $\text{C}_6\text{H}_3(\text{OEt})_2\cdot\text{CO}_2\text{H}$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $\text{C}_6\text{HBr}_2(\text{OH})_2\cdot\text{CO}_2\text{H}$.

20. The term *ether* should be restricted to the oxides of hydrocarbon radicles and their derivatives, and the esters (so-called compound ethers or ethereal salts) should be represented by names similar to those given to metallic salts.

21. When a substituent is one of the groups NH_2 , NHR , NR_2 , NH or NR , its name should end in *ino*; for example, β -aminopropionic acid, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, β -aniline acrylic acid, $\text{NHPh}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$, α -aminopropionic acid, $\text{NH}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$.

22. Compounds of the radicle SO_3H should, whenever possible, be termed sulphonic acids, or failing this, sulpho-compounds; for example, benzenesulphonic acid, sulphobenzoic acid.

23. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteins, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

24. The Collective Index, 4th decade (1903-1912) should be adopted as the standard of reference on questions of nomenclature not provided for in the preceding sections.

Notation.

25. In empirical formulæ the elements are to be given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

26. Equations should be omitted unless essential to the understanding of the results; as a rule, they should not be written on a separate line, but should "run on" with the text.

27. To economise space, it is desirable:

- (a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula.

(b) That formulae should be shortened by the judicious employment of the symbols Me for CH_3 , Et for C_2H_5 , Pr^a for $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$, Pr^s for $\text{CH}(\text{CH}_3)_2$, F for C_6H_5 , Py for $\text{C}_5\text{H}_4\text{N}$, Ac for $\text{CO}\cdot\text{CH}_3$, and Bz for $\text{CO}\cdot\text{C}_6\text{H}_5$.

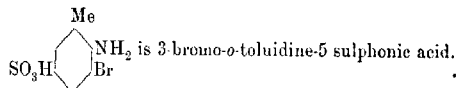
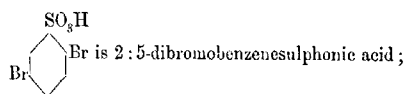
(c) That formulae should be written *in one line* whenever this can be done without obscuring their meaning.

28. In representing the constitution of benzene derivatives, the relative positions of the radicles in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

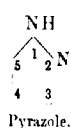
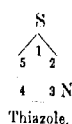
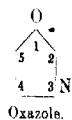
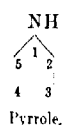
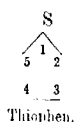
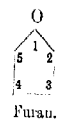
(a) The abbreviations *o*-, *m*-, and *p*-, should be used in place of 1:2- or ortho-, 1:3- or meta-, and 1:4- or para-.

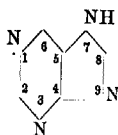
(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radicle of each of these parent substances is to be regarded as in position 1 (compare Collective Index).

(c) Names of substitution derivatives should be given such a way that the position of the substituent indicated by a numeral prefixed; for example:—



29. In representing the constitution of derivatives of other "close chain" hydrocarbons, graphic formulae should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (3rd edition, 1910, pp. 14—26) should be used, of which the following schemes may be regarded as typical:—

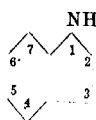




Purine.*



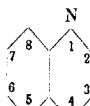
Pyridine.



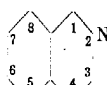
Indole.



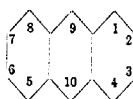
Naphthalene.



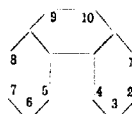
Quinoline.



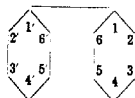
Isoquinoline.



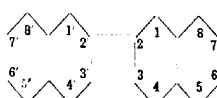
Anthracene.



Phenanthrene.



Diphenyl.

 β -Dinaphthyl.**Manuscript.**

30. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts cannot be accepted unless written on quarto paper (1 x 8 in.).
31. Not more than one abstract must appear on a sheet.
32. When an abstract exceeds a sheet in length, the sheets must be joined together by means of gum at the top left-hand corner.
33. The name of the abstractor must be written diagonally at the left-hand corner of the first sheet of the abstract.

Proofs.

34. Abstractors are expected to read and correct proofs carefully, and to check all formulae and figures against MSS.
35. All proofs, however small, must be returned to the Sub-Editor later than 24 hours after receipt from the printers.

* * The Editor's decision, in all matters connected with the abstracts, must be considered final.

This numbering, proposed originally by E. Fischer, is adopted in the text of the *ikon*.

List of Symbols Recommended by the Working Committee of the International Commission for the Unification of Physico-chemical Symbols (1914). [See Trans., 1921, 119, 502—512.]

1. *Mathematical Symbols.*

	Usual symbol.	Alternative symbol.
Base of natural (Napierian) logarithms	e	
Diameter	d	
Radius	r	
Ratio of circumference to diameter	π	
Summation	Σ	
Variation	δ	
Total differential	d	
Partial differential	∂	

2. *Universal Constants.*

Acceleration due to gravity	g
Mechanical equivalent of heat	J
Avogadro's constant [number of molecules in 1 gram-molecule (mole)]	N
Gas constant per mole	R
Faraday's constant (number of coulombs per gram-equivalent of an ion)	F
Charge on an electron	e

3. *General Physics and Chemistry.*

Length	l
Height	h
Mass	m
Time	t
Volume	v, V
Density (mass per unit volume)	d
Pressure	p, P
Concentration	c, C
Mole fraction	x
Critical constants: pressure, volume, tem- perature (centigrade), temperature (absolute), density	$\left\{ \begin{array}{l} p_c, v_c \\ t_c, T_c \\ d_c \end{array} \right.$
Reduced quantities: pressure, volume, temperature, density	$\left\{ \begin{array}{l} p_r, v_r \\ t_r, T_r, d_r \end{array} \right.$
van der Waals's constants	a, b
Fluidity	ϕ
Viscosity	η
Surface tension	γ
Diffusion coefficient	Δ
Atomic weight	A
Molecular weight	M
Velocity coefficient of reaction	k
Equilibrium constant	$K, (K_e, K_p)$
van't Hoff coefficient	i
Degree of dissociation (electrolytic, thermal, etc.)	

4. Heat and Thermodynamics.

	Usual symbol.	Alternative symbol.
Temperature (centigrade)	t	θ
Temperature (absolute)	T	
Critical temperature	t_c, T_c	
Reduced temperature	t_r, T_r	
Critical solution temperature	t_{cs}, T_{cs}	
Quantity of heat	Q	
Entropy	S	
Specific heat	c	
Specific heat at constant pressure	c_p	
Specific heat at constant volume	c_v	
Ratio of specific heats, $c_p : c_v$	γ	
Molecular heat	C	
Molecular heat at constant pressure	C_p	
Molecular heat at constant volume	C_v	
Latent heat per gram	l	
Latent heat per mole	L	
Maximum work (diminution of free energy)	A	

5. Optics.

Wave-length of light	λ	
Refractive index	n	
Specific refractive power (Gladstone and Dale)	$r_G, [r_G]_\lambda^t$	
Specific refractive power (Lorentz and Lorenz)	$r_L, [r_L]_\lambda^t$	
Molecular refractive power	$\left(\begin{array}{l} R_G, R_L \\ [R_G]_\lambda^t, [R_L]_\lambda^t \end{array} \right)$	
Angle of optical rotation	α	
Specific rotatory power	$[\alpha]$	
Molecular rotatory power	$M[\alpha]$	
Specific magnetic rotation	$[\omega]$	
Molecular magnetic rotation	$M[\omega]$	

6. Electricity and Magnetism.

Quantity of electricity	Q	
Current intensity	I	
Resistance	R	
Electromotive force	E	
Electrode potential, or discharge potential of an ion	E	
Electrode potential referred to the normal hydrogen or normal calomel electrode respectively, the potential of which is taken as zero	E_h, E_c	
Normal potential, <i>i.e.</i> , the electrode potential referred to the normal hydrogen or normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration	${}_0E_h, {}_0E_c$	
Dielectric constant	ϵ	
Conductivity (specific conductance)	κ	
Equivalent conductivity	Λ	
Equivalent conductivity at different dilutions—volumes in litres containing 1 gram-equivalent	$\Lambda_{10}, \Lambda_{20}, \Lambda_{\infty}$	

6. *Electricity and Magnetism*—(continued).

	Usual symbol.	Alternative symbol.
Equivalent conductivity of kation and of anion	Λ_k, Λ_a	
Equivalent conductivity of specified ions...	Λ_K, Λ_{Cl}	
Molecular conductivity	μ	
Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.	U_k, U_a	
Transport number of kation and of anion ...	n_k, n_a	
Magnetic permeability	μ	
Magnetic susceptibility	κ	

List of Symbols, Arranged Alphabetically.

Symbol.	Name of quantity.
A	Atomic weight; maximum work.
a	Van der Waals's constant.
b	Van der Waals's constant.
C	Concentration; molecular heat.
c	Concentration; specific heat.
C_p, C_v	Molecular heat at constant pressure, and at constant volume.
c_p, c_v	Specific heat at constant pressure, and at constant volume.
D	Alternative symbol for density.
d	Diameter; total differential; density.
d_c	Critical density.
d	Reduced density.
E	Electromotive force; electrode potential.
e	Base of Napierian logarithms; charge on an electron.
E_n, E_c	Electrode potential referred to the normal hydrogen or the normal calomel electrode, respectively, the potential of which is taken as zero.
${}_0E_k, {}_0E_c$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration.
F	Faraday's constant (number of coulombs per gram-equivalent of an ion).
g	Acceleration due to gravity.
h	Height.
I	Current.
i	Van't Hoff's coefficient.
J	Mechanical equivalent of heat.
K	Equilibrium constant.
K_o, K_p	Equilibrium constant, when molar concentrations and partial pressures respectively are employed.
k	Velocity coefficient of reaction.
L	Latent heat per mole.
l	Length; latent heat per gram.
M	Molecular weight.
$M[\alpha]$	Molecular rotatory power.
$M[\omega]$	Molecular magnetic rotatory power.
m	Mass.
N	Avogadro's constant (Loschmidt's number) or number of molecules in 1 gram-molecule.
	Refractive index.

List of Symbols, Arranged Alphabetically—(continued).

Symbol.	Name of quantity.
n_k, n_a	Transport number of kation and of anion.
n_r	Refractive index (alternative symbol).
P	Pressure.
p	Pressure.
p_c, p_r	Critical pressure : reduced pressure.
Q	Quantity of heat; quantity of electricity.
R	Gas constant per mole; electrical resistance.
R_0, R_L	Molecular refractive power, according to Gladstone and D��lo, and to Lorentz and Lorenz respectively.
r	Radius.
r_0, r_L	Specific refractive power according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
S	Entropy.
T	Absolute temperature.
T_c	Critical temperature (on the absolute scale).
T_r	Reduced temperature (absolute).
T_s	Critical solution temperature (absolute).
t	Time; temperature (centigrade).
t_c	Critical temperature (centigrade).
t_s	Critical solution temperature (centigrade).
t_r	Reduced temperature (centigrade).
U_k, U_a	Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.
V	Volume.
v	Volume.
v_r, v_r	Critical volume : reduced volume.
W	Electrical resistance (alternative symbol).
x	Mole fraction.
α	Degree of dissociation (electrolytic, thermal, etc.); angle of optical rotation.
$[\alpha]$	Specific rotatory power.
γ	Surface tension; ratio of specific heats.
Δ	Diffusion coefficient.
δ	Variation.
∂	Partial differential.
ϵ	Electrode potential (alternative symbol); dielectric constant.
ϵ_h, ϵ	Electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, the potential of which is taken as zero (alternative symbols).
ϕ^h, ϕ^e	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration (alternative symbols).
η	Viscosity.
θ	Temperature (centigrade), (alternative symbol).
κ	Specific conductance (conductivity); magnetic susceptibility.
Λ	Equivalent conductivity.
$\Lambda_{10}, \Lambda_m, \Lambda_{\infty}$	Equivalent conductivity at different dilutions (volumes in litres containing 1 gram-equivalent).
Λ_k, Λ_a	Equivalent conductivity of kation and of anion.
λ	Wave-length of light.
μ	Molecular conductivity; magnetic permeability
π	Ratio of circumference to diameter.
Σ	Summation.
σ	Surface tension (alternative symbol).
ϕ	Fluidity.
$[\omega]$	Specific magnetic rotation.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

The following is a list of Journals from which abstracts are made (directly or indirectly) by the Chemical Society and the Society of Chemical Industry. The abbreviated titles printed in italics represent Journals abstracted by the Chemical Society, those printed in roman type being abstracted by the Society of Chemical Industry. Of the former Journals those indicated by an asterisk are also abstracted by the Society of Chemical Industry.

ABBREVIATED TITLE.	JOURNAL.
<i>Abh. Böhm. Akad.</i>	Abhandlungen der Böhmischen Akademie.
<i>Abh. Deut. Naturwiss. Med. Ver. Böhmen.</i>	Abhandlungen der Deutschen Naturwissenschaftlichen und Medizinischen Verein, Böhmen.
<i>Acta. Sci. Fennicae</i>	Acta Societatis Scientiarum Fennicae.
<i>Agric. Bull. F. M. S.</i>	Agricultural Bulletin of the Federated Malay States.
<i>Agric. J. India</i>	Agricultural Journal of India.
<i>Agric. Res. Inst., Pusa Rep. (Bull.)</i>	Agricultural Research Institute, Pusa, Report and Bulletin.
<i>Allgem. Z. Bierbrau. u. Malzfabr.</i>	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
<i>Amer. J. Bot.</i>	American Journal of Botany.
<i>Amer. J. Dis. Children</i>	American Journal of Diseases of Children.
<i>Amer. J. Pharm.</i>	American Journal of Pharmacy.
<i>Amer. J. Physiol.</i>	American Journal of Physiology.
<i>Amer. J. Publ. Health</i>	American Journal of Public Health.
<i>*Amer. J. Sci.</i>	American Journal of Science.
<i>Amer. Min.</i>	American Mineralogist.
<i>Anal. Asoc. Quím. Argentina</i>	Anales de la Asociación Química Argentina.
<i>Anal. Fis. Quím.</i>	Anales de la Sociedad Española de Física y Química.
<i>*Analyst</i>	Analyst.
<i>Annalen</i>	Justus Liebig's Annalen der Chemie.
<i>Ann. Bot.</i>	Annals of Botany.
<i>Ann. di Bot.</i>	Annali di Botanica.
<i>Ann. Chim.</i>	Annales de Chimie.
<i>*Ann. Chim. Analyt.</i>	Annales de Chimie Analytique et de Chimie Appliquée.
<i>Ann. Falsif.</i>	Annales des Falsifications.
<i>Ann. hyg. pub. med. legale.</i>	Annales d'hygiène publique et de médecine légale.
<i>Ann. Inst. Pasteur</i>	Annales de l'Institut Pasteur.
<i>Ann. Physik</i>	Annalen der Physik.
<i>Ann. Physique</i>	Annales de Physique.
<i>Ann. R. Staz. Chim. Agrar. Sperim.</i>	Annali della R. Stazione Chimico Agraria Sperimentale di Roma.
<i>Ann. sci. Univ. Jassy</i>	Annales scientifiques de l'Université de Jassy.
<i>Ann. Soc. Geol. Belg.: Publ. rel. au Congo Belge</i>	Annales de la Société géologique de Belgique: Publications relatives au Congo Belge.
<i>Apoth. Zeit.</i>	Apotheker-Zeitung.
<i>Arb. Gebiet. Physik, Math. Chem.</i>	Arbeiten aus dem Gebiete der Physik, Mathematik und Chemie.
<i>Arch. Entw.-mech. Org.</i>	Archiv für Entwicklungsmechanik der Organismen.
<i>Arch. expt. Path. Pharm.</i>	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. Farm. sperim. Sci. aff.</i>	Archivio di Farmacologia sperimentale e Scienze affini.

ABBREVIATED TITLE.	JOURNAL.
<i>Arch. Fisiol.</i>	Archivio di Fisiologia.
<i>Arch. Int. Med.</i>	The Archives of Internal Medicine.
<i>Arch. Ital. Biol.</i>	Archives italiennes de Biologie.
<i>Arch. Med. Pharm. milit.</i>	Archives de Médecine et de Pharmacie militaires.
<i>Arch. Néerland.</i>	Archives Néerlandaises de sciences exactes et naturelles
<i>Arch. Néerland. physiol.</i>	Archives Néerlandaises de physiologie de l'homme et des animaux.
* <i>Arch. Pharm.</i>	Archiv der Pharmazie.
<i>Arch. Sci. phys. nat.</i>	Archives des Sciences physiques et naturelles.
<i>Arch. Suikerind. Ned. Indië</i>	Archief voor de Suikerindustrie in Nederlandsch-Indië.
<i>Arkiv Kem. Min. Geol.</i>	Arkiv för Kemi, Mineralogi och Geologi.
<i>Astrophys. J.</i>	Astrophysical Journal.
* <i>Atti R. Accad. Lincei</i>	Atti della Reale Accademia Nazionale dei Lincei.
<i>Atti R. Accad. Sci. Torino</i>	Atti della Reale Accademia delle Scienze di Torino.
<i>Atti R. Ist. Veneto Sci.</i>	Atti del Reale Istituto Veneto di Scienze, Lettere ed Arti.
<i>Aust. Pharm. Notes</i>	Australian Pharmaceutical Notes and News
<i>Beitr. Min. Japan</i>	Beiträge zur Mineralogie von Japan.
<i>Berg. Hüttenm. Rundsch.</i>	Berg- und Hüttenmännisches Rundschau.
* <i>Ber.</i>	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Deut. bot. Ges.</i>	Berichte der Deutschen botanischen Gesellschaft.
* <i>Ber. Deut. pharm. Ges.</i>	Berichte der Deutschen pharmazeutischen Gesellschaft.
<i>Ber. Oberhess. Ges. Natur. Heilkunde.</i>	Berichte der Oberhessischen Gesellschaft für Natur- und Heilkunde zu Giessen.
<i>Ber. Ohara Inst. landw. Forsch.</i>	Berichte des Ohara Instituts für landwirtschaftliche Forschungen
<i>Ber. Sachs. Akad. Wiss.</i>	Berichte über die Verhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig.
<i>Berlin. Klin. Woch.</i>	Berliner Klinische Wochenschrift.
* <i>Bied. Zentr.</i>	Biedermann's Zentralblatt.
* <i>Biochem. J.</i>	Biochemical Journal.
* <i>Biochem. Z.</i>	Biochemische Zeitschrift.
<i>Bl. of Trade J.</i>	Board of Trade Journal.
<i>Bol. Acad. Nac. Ciencias, Córdoba</i>	Boletín de la Academia Nacional de Ciencias, Córdoba.
* <i>Boll. Chim. farm.</i>	Bolletino Chimico farmaceutico.
<i>Boll. Soc. Geol. Ital.</i>	Bolletino della Società Geologica Italiana.
<i>Boll. Soc. Med.-Chirurg.</i>	Bolletino della Società Medico-Chirurgica, Pavia.
<i>Bot. Centr.</i>	Botanisches Centralblatt.
<i>Bot. Gaz.</i>	Botanical Gazette.
<i>Brass. Malt.</i>	Brasserie et Malterie.
<i>Brau- u. Malzind.</i>	Brau- u. Malzindustrie.
<i>Braunkohle</i>	Braunkohle.
* <i>Brennstoff-Chem.</i>	Brennstoff-Chemie.
<i>Brewers' J.</i>	Brewers' Journal.
<i>Brit. J. Phot.</i>	British Journal of Photography.
<i>Brit. Med. J.</i>	British Medical Journal.
<i>Brit. Pat.</i>	British Patent.
<i>Buletinul Chim.</i>	Buletinul Chimie.
<i>Bul. Soc. Chim. România</i>	Buletinul Societății de Chimie din România.
<i>Bul. Soc. Romane Stiin.</i>	Buletinul Societății Române de Științe.
<i>Bull. Acad. roy. Belg.</i>	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Acad. Sci. Roumaine</i>	Bulletin de la Section Scientifique de l'Académie Roumaine.
<i>Bull. Assoc. Chim. Sucr.</i>	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.

ABBREVIATED TITLE.	JOURNAL.
Bull. Bureau of Standards (U.S.A.).	Bulletin of the Bureau of Standards (U.S.A.).
Bull. Com. Géol. Finlande.	Bulletin de la Commission Géologique de Finlande.
Bull. Forest Exp. Stat. Meguro.	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
Bull. gén. Thérap.	Bulletin général de Thérapie médicale, chirurgicale, obstétricale.
Bull. Géol. d'Alsace.	Bulletin du Service de la Carte Géologique d'Alsace et de Lorraine.
Bull. Geol. Inst. Univ. Upsala.	Bulletin of the Geological Institution of the University of Upsala.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Geol. Survey, U.S.A.	Bulletin of the U.S. Geological Survey.
Bull. Geol. Survey, West Australia.	Bulletin of the Geological Survey, West Australia.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Indian Ind. Lab.	Bulletin of Indian Industries and Labour.
Bull. Johns Hopkins Hospital.	Bulletin of the Johns Hopkins Hospital.
Bull. School Mines and Met., Univ. Missouri.	Bulletin of the School of Mines and Metallurgy, University of Missouri.
Bull. Sci. Pharmacol.	Bulletin des Sciences Pharmaceutiques.
*Bull. Soc. chim.	Bulletin de la Société chimique de France.
*Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.
Bull. Soc. d'Encour.	Bulletin de la Société d'Encouragement pour l'Industrie Nationale.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. Franç. Phot.	Bulletin de la Société Française de Photographie.
Bull. Soc. Ind. Mulhouse.	Bulletin de la Société Industrielle de Mulhouse.
Bull. Soc. Ind. Nord.	Bulletin de la Société Industrielle du Nord de la France.
Bull. Soc. Oural. Sci. Nat.	Bulletin de la Société Ouralienne des Amateurs des Sciences Naturelles à Catherineberg.
Bull. Soc. Pharm. Bordeaux.	Bulletin des Travaux de la Société de Pharmacie de Bordeaux.
Bull. Wellcome Trop. Res. Lab.	Bulletin of the Wellcome Tropical Research Laboratory.
Cairo Sci. J.	Cairo Scientific Journal.
Canada Dept. Mines Publ.	Canada Department of Mines Publications.
*Canadian Chem. Met.	Canadian Chemistry and Metallurgy.
Canadian Med. Assoc. J.	Canadian Medical Association Journal.
Caoutchouc et Gutta-Percha	Le Caoutchouc et le Gutta-Percha.
Casopis. Math. Fysiky	Casopis pro pěstování Matematiky a Fysiky.
Cellulosechem.	Cellulosechemie.
*Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Paläontologie.
Ch. of Comm. J.	Chamber of Commerce Journal.
Chem. App.	Chemische Apparatur.
Chem. Erde	Chemie der Erde.
Chem. Ind.	Chemische Industrie.
Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Česká chemická Společnost pro Vědu a Průmysl."
*Chem. and Met. Eng.	Chemical and Metallurgical Engineering.
*Chem. News	Chemical News.
Chem. Trade J.	Chemical Trade Journal.

ABBREVIATED TITLE.	JOURNAL.
Chem. Umschau . . .	Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse, und Harze.
*Chem. Weekblad . . .	Chemisch Weekblad.
*Chem. Ztg.	Chemiker-Zeitung.
*Chem. Zentr.	Chemisches Zentralblatt.
Chem. and Drug.	Chemist and Druggist.
*Chem. et Ind.	Chimie et Industrie.
Collegium	Collegium.
*Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
Comptes rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux du Laboratoire Carlsberg.
D. R. P.	Deutsches Reichs-Patent.
Dept. Chem. S. Australia, Bull.	Department of Chemistry, South Australia, Bulletins.
Deut. med. Woch.	Deutsche medizinische Wochenschrift.
Econ. Geol.	Economic Geology.
Econ. Proc. Roy. Dubl. Soc.	Economic Proceedings of the Royal Dublin Society.
Engineering	Engineering.
Eng. and Min. J.	Engineering and Mining Journal.
Exper. Stat. Rec.	Experiment Station Record.
Farben-Ztg.	Farben-Zeitung.
Fermentforsch.	Fermentforschung.
Feuerungstechnik	Feuerungstechnik.
Flora	Flora.
Földtani Közöny	Földtani Közöny.
Fr. Pat.	French Patent.
Gas J.	Gas Journal.
Gas World	Gas World.
*Gazzetta	Gazzetta chimica italiana.
Geol. För. Förh.	Geologiska Föreningens i Stockholm Förhandlingar.
Geol. Mag.	Geological Magazine.
Gerber	Gerber.
*Giorn. Chim. Ind. Appl.	Giornale di Chimica Industriale ed Applicata.
Gummi-Ztg.	Gummi-Zeitung.
Handl. Vijft. Nat.	Handelingen van het Vijftende Natuur.
Hawaii Agric. Exp. Stat. Bull.	Hawaii Agricultural Experiment Station Bulletins.
Heart	Heart.
Helv. Chim. Acta.	Helvetica Chimica Acta.
Indian J. Med. Res.	Indian Journal of Medical Research.
India-rubber J.	India-rubber Journal.
Int. Rev. Sci. Pract. Agric.	International Review of the Science and Practice of Agriculture.
Int. Sugar J.	International Sugar Journal.
Iron Steel Inst. Carnegie Schol. Mem.	Iron and Steel Institute, Carnegie Scholarship Memoirs.
Jahrb. Geol. Reichsanst.	Jahrbuch der geologischen Reichsanstalt.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie, Beilage-Band.
Jahrb. Radioaktiv. Elek. tronik.	Jahrbuch der Radioaktivität und Elektronik.
Jahrb. wiss. Bot.	Jahrbuch für wissenschaftliche Botanik.
Jahresber. Ges. vaterl. Kultur.	Jahresbericht der schlesischen Gesellschaft für vaterländische Kultur.

14 JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
<i>Jernk. Ann.</i>	Jern-kontorets Annaler.
* <i>J. Agric. Res.</i>	Journal of Agricultural Research.
* <i>J. Agric. Sci.</i>	Journal of Agricultural Science.
<i>J. Am.-r. Ceram. Soc.</i>	Journal of the American Ceramic Society.
* <i>J. Amer. Chem. Soc.</i>	Journal of the American Chemical Society.
<i>J. Amer. Leather Chem. Assoc.</i>	Journal of the American Leather Chemists' Association.
<i>J. Amer. Med. Assoc.</i>	Journal of the American Medical Association.
<i>J. Assoc. Off. Agric. Chem.</i>	Journal of the Association of Official Agricultural Chemists.
* <i>J. Biol. Chem.</i>	Journal of Biological Chemistry.
<i>J. Canad. Min. Inst.</i>	Journal of the Canadian Mining Institute.
<i>J. Chem. Ind. Tokyo</i>	See Kōgyō-Kwagaku-Zasshi.
<i>J. Chem. Met. Soc. S. Africa</i>	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
<i>J. Chem. Soc. Japan.</i>	Journal of the Chemical Society of Japan. (Nippon Kwagaku Kwai Shi.)
<i>J. Chim. physique</i>	Journal de Chimie physique.
<i>J. Coll. Agric. Hokkaido</i>	Journal of the College of Agriculture, Hokkaido Imperial University, Japan.
<i>J. Coll. Agric. Tokyo</i>	Journal of the College of Agriculture, Imperial University of Tokyo, Japan.
<i>J. Coll. Eng. Tokyo</i>	Journal of the College of Engineering, Imperial University of Tokyo.
* <i>J. Coll. Sci. Tokyo</i>	Journal of the College of Science, Imperial University of Tokyo.
<i>J. Exp. Med.</i>	Journal of Experimental Medicine.
* <i>J. Franklin Inst.</i>	Journal of the Franklin Institute.
<i>J. Gasbeleucht.</i>	Journal für Gasbeleuchtung und Wasserversorgung.
<i>J. gen. Physiol.</i>	Journal of general Physiology.
<i>J. Genetics</i>	Journal of Genetics.
<i>J. Geol.</i>	Journal of Geology.
<i>J. Geol. Soc. Tokyo</i>	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
<i>J. Hygiene</i>	Journal of Hygiene.
* <i>J. Ind. Eng. Chem.</i>	Journal of Industrial and Engineering Chemistry.
<i>J. Indian Ind. Lab.</i>	Journal of Indian Industries and Labour.
* <i>J. Indian Inst. Sci.</i>	Journal of the Indian Institute of Science.
<i>J. Inst. Brewing</i>	Journal of the Institute of Brewing.
<i>J. Inst. Metals</i>	Journal of the Institute of Metals.
<i>J. Inst. Petroleum Tech.</i>	Journal of the Institution of Petroleum Technologists.
<i>J. Iron and Steel Inst.</i>	Journal of the Iron and Steel Institute.
<i>J. Landw.</i>	Journal für Landwirtschaft.
<i>J. Marine Biol. Assoc. U.K.</i>	Journal of the Marine Biological Association of the United Kingdom.
<i>J. Med. Res.</i>	Journal of Medical Research.
<i>J. Min. Agric.</i>	Journal of the Ministry of Agriculture.
<i>J. Path. Bact.</i>	Journal of Pathology and Bacteriology.
<i>J. Opt. Soc. Amer.</i>	Journal of the Optical Society of America.
* <i>J. Pharm. Chin.</i>	Journal de Pharmacie et de Chimie.
<i>J. Pharm. Expt. Ther.</i>	Journal of Pharmacology and Experimental Therapeutics.
<i>J. Pharm. Soc. Japan</i>	Journal of the Pharmaceutical Society of Japan (Yakugakuzasshi).
* <i>J. Physical Chem.</i>	Journal of Physical Chemistry.
<i>J. Physiol.</i>	Journal of Physiology.
<i>J. Physiol. Path. gén.</i>	Journal de Physiologie et de Pathologie générale.
<i>J. Phys. Radium</i>	Journal de Physique et le Radium.

ABBREVIATED TITLE.	JOURNAL.
* <i>J. pr. Chem.</i>	Journal für praktische Chemie.
<i>J. Proc. Asiatic Soc. Bengal.</i>	Journal and Proceedings of the Asiatic Society of Bengal.
<i>J. Roy. Agric. Soc.</i>	Journal of the Royal Agricultural Society.
<i>J. Roy. Army Med. Corps.</i>	Journal of the Royal Army Medical Corps.
<i>J. Roy. Hort. Soc.</i>	Journal of the Royal Horticultural Society.
<i>J. Roy. Soc. New South Wales.</i>	Journal and Proceedings of the Royal Society of New South Wales.
<i>J. Roy. Soc. West Australia.</i>	Journal of the Royal Society of West Australia.
* <i>J. Russ. Phys. Chem. Soc.</i>	Journal of the Physical and Chemical Society of Russia.
<i>J. Scot. Met. Soc.</i>	Journal of the Scottish Meteorological Society.
<i>J. Soc. Arts</i>	Journal of the Royal Society of Arts.
<i>J. Soc. Dyers and Col.</i>	Journal of the Society of Dyers and Colourists.
<i>J. Soc. Leather Trades Chem.</i>	Journal of the Society of Leather Trades Chemists.
<i>J. Soc. Glass Technology.</i>	Journal of the Society of Glass Technology.
[<i>J. S. African Assoc. Anal. Chem.</i>]	[Journal of the South African Association of Analytical Chemists.]
<i>Changed 1922 to</i>	
<i>J. S. African Chem. Inst.</i>	Journal of the South African Chemical Institute.
<i>J. Textile Inst.</i>	Journal of the Textile Institute.
<i>J. Usines Gaz</i>	Journal des Usines à Gaz.
<i>J. Washington Acad. Sci.</i>	Journal of the Washington Academy of Science.
<i>J. West Scotland Iron Steel Inst.</i>	Journal of the West of Scotland Iron and Steel Institute.
<i>K. Svenska Vet. Akad. Handl.</i>	Kongliga Svenska Vetenskaps Akademiens Handlingar.
Kentucky Exp. Stat. Bull.	Kentucky Experimental Station, Bulletin.
Keram. Rundsch. . . .	Keramisch Rundschau.
Kew Bull. . . .	Kew Bulletin.
Kōgyō-Kwagaku-Zasshi (J. Chem. Ind. Japan).	Kōgyō-Kwagaku-Zasshi (Journal of Chemical Industry, Japan).
* <i>Kolloid Z.</i>	Kolloid Zeitschrift.
* <i>Koll. Chem. Beihefte</i>	Kolloid-chemische Beihefte.
<i>Kosmos</i>	Kosmos (Lemberg).
<i>Kuhn-Archiv</i>	Kuhn-Archiv.
<i>Kunststoffe</i>	Kunststoffe.
<i>Lancet</i>	The Lancet.
<i>Landw. Jahrb.</i>	Landwirtschaftliche Jahrbücher.
<i>Landw. Versuchs.-Stat.</i>	Die landwirtschaftlichen Versuchs Stationen.
<i>Leather Trades Rev.</i>	Leather Trades Review.
<i>Louisiana Bull.</i>	Louisiana Bulletin.
<i>Louisiana Planter</i>	Louisiana Planter.
<i>Lunds Univ. Årsskr.</i>	Lunds Universitets Årsskrift.
<i>Math. és Termész. Ért.</i>	Mathematikai és Természettudományi Értesítő, Budapest.
<i>Medd. K. Vetenskapsakad. Nobel-Inst.</i>	Meddelanden från Kongl. Vetenskapsakademiens Nobel-Institut.
<i>Medd. om Grönland</i>	Meddelelser om Grönland.
<i>Med. Genes. Lab. Weltevreden.</i>	Mededeelingen uit het Geneeskundig Laboratorium te Weltevreden.
<i>Med. Chron.</i>	Medical Chronicle.
<i>Med. Klinik</i>	Medizinische Klinik.
<i>Mem. Accad. Lincei</i>	Memorie della Reale Accademia dei Lincei.
<i>Mem. Accad. Sci. Torino</i>	Memorie della Reale Accademia delle Scienze di Torino.
<i>Mem. Coll. Sci. Kyōto</i>	Memoirs of the College of Science, Kyōto Imperial University.
<i>Mem. Coll. Sci. and Eng. Kyōto Imp. Univ.</i>	Memoirs of the College of Science and Engineering, Kyōto Imperial University.

ABBREVIATED TITLE.	JOURNAL.
Mem. Dept. Agric. India . . .	Memoirs of the Department of Agriculture in India.
Mem. Manchester Phil. Soc. . .	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mem. Soc. Ing. Civ.	Mémoires de la Société des Ingénieurs Civils de France.
Mem. Soc. Toscana Sci. Nat. . .	Memorie della Società Toscana di Scienze naturali residente in Pisa.
Metall u. Erz	Metall und Erz.
Metrop. Water Bd. Rep. . . .	Metropolitan Water Board Reports.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Mitt. Materialprüf.	Mittheilungen aus dem Materialprüfungsamt zu Gross-Lichterfelde West.
Mitt. med. Ges. Tokyo	Mittheilungen der medizinischen Gesellschaft zu Tokyo.
Mitt. Naturforsch. Ges. Halle.	Mittheilungen der Naturforschenden Gesellschaft zu Halle.
Mitt. Path. Inst. K. Univ. Japan.	Mittheilungen aus dem pathologischen Institut der Kaiserlichen Universität zu Sendai, Japan.
*Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Monatsh. Math. Physik	Monatshefte für Mathematik und Physik.
*Mon. Sci.	Moniteur Scientifique.
Month. Not. Roy. Astr. Soc. . .	Monthly Notices of the Royal Astronomical Society, London.
Münch. med. Woch.	Münchener medizinische Wochenschrift.
Nachr. Ges. Wiss. Göttingen.	Nachrichten der Gesellschaft der Wissenschaften zu Göttingen.
Nature	Nature.
Naturwiss.	Die Naturwissenschaften.
Naturw. Rdsch.	Naturwissenschaftliche Rundschau.
New York Agr. Expt. Sta. Bull.	New York Agricultural Experiment Station Bulletins.
New Zealand Dominion Laby. Rept.	New Zealand Dominion Laboratory Reports.
New Zealand Jnl. of Science and Technology	New Zealand Journal of Science and Technology.
Nippon Kwagaku Kwaï Shi (J. Chem. Soc. Japan).	Nippon Kwagaku Kwa Shi (Journal of the Chemical Society of Japan).
Nova Acta Soc. Sci.	Nova Acta Regiæ Societatis Scientiarum Upsaliensis.
Nuovo Cim.	Il Nuovo Cimento.
Öfvers. Finska Vet.-Soc. . . .	Öfversigt af Finska Vetenskaps-Societätens Förhandlingar, Helsingfors.
*Oesterr. Chem.-Zeit.	Oesterreichische Chemiker-Zeitung.
Oil and Colour Trades J. . . .	Oil and Colour Trades Journal.
Oil, Paint, and Drug Rep. . . .	Oil, Paint, and Drug Reporter.
Oversigt Danske Vid. Selsk. . . .	Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlingar.
Paper	Paper.
Papierfabr.	Papier-Fabrikant.
Perf. and Essent. Oil Rec. . . .	Perfumery and Essential Oil Record.
Per. spis. Sofia	Periodicesko spisanie Sofia.
Petroleum Age.	Petroleum Age, including Petroleum.
Pfuger's Archiv	Archiv für die gesamte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
*Pharm. Weekblad	Pharmaceutisch Weekblad.
*Pharm. Zentr.-h.	Pharmazeutische Zentrallhalle.

ABBREVIATED TITLE.	JOURNAL.
<i>Phil. Mag.</i>	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society of London.
Philippine J. Sci. . . .	Philippine Journal of Science.
Phot. J.	Photographic Journal.
Phot. Korr.	Photographische Korrespondenz.
<i>Physical Rev.</i>	Physical Review.
<i>Physikal. Z.</i>	Physikalische Zeitschrift.
<i>Proc. Amer. Phil. Soc.</i> . .	Proceedings of the American Philosophical Society.
<i>Proc. Amer. Physiol. Soc.</i> .	Proceedings of the American Physiological Society.
* <i>Proc. Amer. Soc. Biol. Chem.</i>	Proceedings of the American Society of Biological Chemists.
<i>Proc. Amer. Soc. Civ. Eng.</i>	Proceedings of the American Society of Civil Engineers.
<i>Proc. Amer. Soc. Testing Materials</i>	Proceedings of American Society for Testing Materials.
<i>Proc. Austral. Inst. Min. Met.</i>	Proceedings of the Australasian Institute of Mining and Metallurgy.
<i>Proc. Camb. Phil. Soc.</i> . .	Proceedings of the Cambridge Philosophical Society.
<i>Proc. Durham Phil. Soc.</i> . .	Proceedings of the Durham Philosophical Society.
<i>Proc. Eng. Soc. W. Pa.</i> . .	Proceedings of the Engineers' Society of Western Pennsylvania.
<i>Proc. Inst. Civ. Eng.</i> . . .	Proceedings of the Institution of Civil Engineers.
<i>Proc. Inst. Mech. Eng.</i> . .	Proceedings of the Institution of Mechanical Engineers.
* <i>Proc. K. Akad. Wetensch. Amsterdam.</i>	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
<i>Proc. Nat. Acad. Sci.</i> . . .	Proceedings of the National Academy of Sciences.
<i>Proc. Nova Scotia Inst. Sci.</i>	Proceedings of the Nova Scotia Institute of Science.
<i>Proc. Phil. Soc. Glasgow</i> . .	Proceedings of the Glasgow Philosophical Society.
<i>Proc. Physical Soc.</i>	Proceedings of the Physical Society of London.
<i>Proc. Physiol. Soc.</i>	Proceedings of the Physiological Society.
<i>Proc. Roy. Inst.</i>	Proceedings of the Royal Institution of Great Britain.
<i>Proc. Roy. Irish Acad.</i> . . .	Proceedings of the Royal Irish Academy.
* <i>Proc. Roy. Soc.</i>	Proceedings of the Royal Society.
<i>Proc. Roy. Soc. Edin.</i> . . .	Proceedings of the Royal Society of Edinburgh.
<i>Proc. Roy. Soc. Med.</i>	Proceedings of the Royal Society of Medicine.
<i>Proc. Roy. Soc. Queensland</i> .	Proceedings of the Royal Society of Queensland.
<i>Proc. Roy. Soc. Tasmania</i> . .	Proceedings of the Royal Society of Tasmania.
<i>Proc. Soc. Exp. Biol. Med.</i> . .	Proceedings of the Society for Experimental Biology and Medicine.
<i>Proc. U.S. Nat. Mus.</i>	Proceedings of the United States National Museum.
<i>Proc. verb. Soc. Toscana Sci. Nat.</i>	Processi verbali Società Toscana di Scienze Naturali.
Pulp and Paper Magazine . .	Pulp and Paper Magazine of Canada.
<i>Quart. J. Geol. Soc.</i>	Quarterly Journal of the Geological Society.
<i>Quart. J. Med.</i>	Quarterly Journal of Medicine.
<i>Radium in Biol. Heilkunde</i> . .	Radium in Biologie und Heilkunde.
<i>Rec. Australian Mus.</i>	Records of the Australian Museum.
<i>Rec. trav. bot. Néerland.</i> . .	Recueil des travaux botaniques Néerlandaises.
* <i>Rec. trav. chim.</i>	Recueil des travaux chimiques des Pays-Bas.
<i>Rend. Accad. Sci. Fis. Mat. Napoli.</i>	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
<i>Rend. Ist. Lomb. Sci. Lett.</i> . .	Rendiconti dell' Reale Istituto Lombardo di Scienze e Lettere.
<i>Rep. Aust. Assoc. Sci.</i>	Report of the Australian Association for the Advancement of Science.
<i>Rep. Brit. Assoc.</i>	Report of the British Association for the Advancement of Science.

ABBREVIATED TITLE.	JOURNAL.
<i>Rev. Chim.</i> . . .	Revue chimique . . . <i>Oficijelni organ udruženja Jugoslavenskih Kemikara.</i>
<i>Rev. gén. Bot.</i> . . .	Revue générale de Botanique.
<i>Rev. Gén. Mat. Col.</i> . . .	Revue Générale des Matières Colorantes.
<i>Rev. Mét.</i> . . .	Revue de Métallurgie.
<i>Rev. Real Acad. Ciencias exact. Madrid.</i>	Revista de la Real Academia de Ciencias exactas, Físicas y Naturales de Madrid.
<i>Riv. Min. Crist. Ital.</i> . . .	Rivista di Mineralogia e Cristallografia Italiana.
* <i>Roczniki Chemji</i> . . .	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
<i>Sbornik Klubu Pri.</i> . . .	Sbornik Klubu Přírodovědeckého (Prague).
<i>Schweiz. Apoth. Zeit.</i> . . .	Schweizerische Apotheker Zeitung.
<i>Schweiz. Chem. Zeit.</i> . . .	Schweizerische Chemiker Zeitung.
<i>Science</i> . . .	Science.
<i>Scient. Amer.</i> . . .	Scientific American.
* <i>Sci. Ind. Rep. Roure-Bertrand Fils.</i>	Scientific and Industrial Reports of Roure-Bertrand Fils.
<i>Sci. Proc. Roy. Dubl. Soc.</i> . . .	Scientific Proceedings of the Royal Dublin Society.
<i>Sci. Rep. Tôhoku Imp. Univ.</i>	Science Reports, Tôhoku Imperial University.
<i>Sci. Trans. Roy. Dubl. Soc.</i>	Scientific Transactions of the Royal Dublin Society.
<i>Seifensied. Ztg.</i> . . .	Seifensieder Zeitung.
<i>Sitzungsber. Akad. München.</i>	Sitzungsberichte der bayerischen Akademie der Wissenschaften zu München.
<i>Sitzungsber. Akad. Wiss. Wien.</i>	Sitzungsberichte der Akademie der Wissenschaften, Wien.
<i>Sitzungsber. Ges. Naturwiss. Marburg.</i>	Sitzungsberichte der Gesellschaft zur Beförderung der gesamten Naturwissenschaften in Marburg.
<i>Sitzungsber. Heidelberger Akad. Wiss.</i>	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
<i>Sitzungsber. Med. Naturwiss. Ges. Münster.</i>	Sitzungsberichte der Medizinisch-Naturwissenschaftlichen Gesellschaft zu Münster-in-Westfalen.
<i>Sitzungsber. Naturforsch. Ges. Rostock.</i>	Sitzungsberichte der Naturforschenden Gesellschaft zu Rostock.
<i>Sitzungsber. phys. med. Ges. Erlangen</i>	Sitzungsberichte der physikalisch-medizinischen Gesellschaft zu Erlangen.
<i>Sitzungsber. Preuss. Akad. Wiss. Berlin.</i>	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
<i>Skand. Arch. Physiol.</i> . . .	Skandinavisk Archiv för Physiologie.
<i>Smithsonian Miscell. Coll.</i> . . .	Smithsonian Miscellaneous Collections.
* <i>Soil Sci.</i> . . .	Soil Science.
<i>South African J. Ind.</i> . . .	South African Journal of Industries.
<i>South African J. Sci.</i> . . .	South African Journal of Science.
<i>Sprechsaal</i> . . .	Sprechsaal.
<i>Stahl u. Eisen</i> . . .	Stahl und Eisen.
<i>Staz. sper. agr. ital.</i> . . .	Stazioni sperimentali agrarie italiane.
<i>Strahlenther.</i> . . .	Strahlentherapie.
<i>Suom. Tied. Toim.</i> . . .	Suomalaisen Tiedekatemian Toimituksia.
<i>Svensk Kem. Tidskr.</i> . . .	Svensk Kemik Tidskrift.
<i>T.</i> . . .	Transactions of the Chemical Society.
<i>Tech. Rep. Tôhoku Imp. Univ.</i>	Technology Reports of the Tôhoku Imperial University, Sendai, Japan.
<i>Tekn. Tidsk.</i> . . .	Teknisk Tidskrift
<i>Textilber.</i> . . .	Textilberichte über Wissenschaft, Industrie und Handel.
<i>Ther. Gegenw.</i> . . .	Die Therapie der Gegenwart.
<i>Ther. Monatsh.</i> . . .	Therapeutische Half-Monatshefte.
<i>Times Eng. Suppl.</i> . . .	Times Engineering Supplement.
<i>Töndind.-Zeit.</i> . . .	Töndindustrie-Zeitung.

ABBREVIATED TITLE.	JOURNAL.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Amer. Inst. Chem. Edg.	Transactions of the American Institute of Chemical Engineers.
Trans. Amer. Inst. Metals.	Transactions of the American Institution of Metals.
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Ceram. Soc.	Transactions of the Ceramic Society.
*Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Min. and Met.	Transactions of the Institution of Mining and Metallurgy.
Tr. N. Eng. Inst. Min. and Met.	Transactions of the North of England Institute of Mining and Metallurgy.
Trans. New Zealand Inst.	Transactions of the New Zealand Institute.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Trans. Roy. Soc. Canada.	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
Trans. Roy. Soc. Sth. Africa.	Transactions of the Royal Society of South Africa.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mittheilungen.
U.S. Bureau of Mines, Bull. and Tech. Papers.	United States Bureau of Mines, Bulletins and Technical Papers.
U.S. Bureau Plant Ind.	United States Bureau of Plant Industry.
U.S. Comm. Rept.	United States Commerce Reports, Daily Consular and Trade Reports.
U.S. Dept. Agric. Bull.	United States Department of Agriculture Bulletins.
U.S. Hyg. Labor. Bull.	United States Hygienic Laboratory Bulletins.
U.S. Pat.	United States Patent.
Univ. Illinois Bull.	University of Illinois Bulletins.
Utah Agric. Coll. Exper. Stat. Bull.	Utah Agricultural College Experiment Station Bulletins.
Verh. Grol. Reichsanst. Wien.	Verhandlungen der geologischen Reichsanstalt in Wien.
Verh. Ges. deut. Naturforsch. Aerzte.	Verhandlungen der Gesellschaft deutscher Naturforscher und Aerzte.
Verh. Naturhist. med. Ver. Heidelberg.	Verhandlungen des naturhistorisch-medizinischen Vereins zu Heidelberg.
Verh. Naturhist. Rheintl.	Verhandlungen des naturhistorischen Vereins der preussischen Rheinlande und Westfalens.
Verh. Physiol. Ges. Berlin.	Verhandlungen der Physiologischen Gesellschaft zu Berlin.
Verh. Schweiz. Nat. Ges.	Verhandlungen der Schweizerischen Naturforschenden Gesellschaft, Basel.
Vict. Mem. Mus. Geol. Survey, Canada.	Victoria Memorial Museum Geological Survey of Canada, Bulletin.
Videnskab. Skrifter.	Skrifter udgivne af Videnskabselskabet i Kristiania.
Wiener Klin. Woch.	Wiener Klinische Wochenschrift.
Wiss. Abhandl. Physikal.-Tech. Reichsanst.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Wiss. Veröff. Siemens Konz.	Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern.
Wochbl. Papierfabr.	Wochenblatt für Papierfabrikation.
Woch. f. Bran.	Wochenschrift für Brauerei.
*Yakugakuzasshi (J. Pharm. Soc. Japan).	Yakugakuzasshi (Journal of the Pharmaceutical Society of Japan).
Z. allg. Physiol.	Zeitschrift für allgemeine Physiologie.
*Z. anal. Chem.	Zeitschrift für analytische Chemie.

ABBREVIATED TITLE.	JOURNAL.
*Z. angew. Chem. . . .	Zeitschrift für angewandte Chemie.
*Z. anorg. Chem. . . .	Zeitschrift für anorganische und allgemeine Chemie.
Z. Biol.	Zeitschrift für Biologie.
Z. deut. Geol. Ges. . . .	Zeitschrift der deutschen Geologischen Gesellschaft.
Z. deut. Oel-Fett Ind. . .	Zeitschrift der deutschen Oel- und Fett- Industrie.
*Z. Elektrochem. . . .	Zeitschrift für Elektrochemie.
Z. exp. Path. Ther. . . .	Zeitschrift für experimentelle Pathologie und Therapie.
Z. ges. Brauw.	Zeitschrift für das gesamte Brauwesen.
Z. ges. exp. Med.	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Schiess- u. Sprengstoffw. . . .	Zeitschrift für das gesamte Schiess- und Sprengstoffwesen.
Z. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten.
Z. Immunit.	Zeitschrift für Immunitätsforschung und experimentelle Therapie.
Z. Instrument.	Zeitschrift für Instrumentenkunde.
Z. Kryst.	Zeitschrift für Krystallographie.
Z. Leder. Gerb. Chem. . .	Zeitschrift für Leder- und Gerberei-Chemie.
Z. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Z. Physik.	Zeitschrift für Physik.
*Z. physikal. Chem. . . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physikal. Chem. Unterr.	Zeitschrift für den physikalischen und Chemischen Unterricht.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. prakt. Geol.	Zeitschrift für praktische Geologie.
*Z. Sauerstoff Stickstoff Ind.	Zeitschrift für Sauerstoff und Stickstoff Industrie.
Z. Spiritusind.	Zeitschrift für Spiritusindustrie.
Z. Unters. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Z. wiss. Mikrosk.	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
*Z. wiss. Photochem. . . .	Zeitschrift für wissenschaftliche Photographie, Photo-physik und Photochemie.
*Z. Zuckerind. Čechoslov.	Zeitschrift für Zuckerindustrie der Čechoslovakischen Republik.
Zentr. Zuckerind.	Zentralblatt für Zuckerindustrie.

JOURNAL OF THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

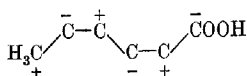
PART I.

Organic Chemistry.

The Oscillation of Physical Constants in Homologous Series. HERMANN PAULY (*Z. anorg. Chem.*, 1921, **119**, 271—291).—The theories put forward by Tammann (A., 1920, ii, 285) and Cuy (A., 1921, ii, 429) to explain the oscillation in the numerical values of different physical properties in homologous series are criticised and an alternative explanation is suggested. A review of the existing data leads to the conclusion that the end groups of the carbon chain and their relationship to each other, especially in the spatial sense, have an important influence on the physical properties. In the fatty acid series, the odd members have proportionately lower molecular volumes and at the same time lower melting points than the even members. It is probable that in the open straight chain compounds the carbon atoms form a zigzag chain, and it follows that when the number of carbon atoms is even the end atoms are relatively farther apart than when the number is odd. The difference is of the "syn" and "anti" type, the odd members having a "syn" structure with low molecular volume and low melting point, the even members the "anti" structure with higher molecular volume and melting point. The odd members, however, have the higher boiling points. Similarly, the solubilities and molecular heats in the fatty acid series oscillate in the opposite direction to the molecular volume.

A special type of oscillation is exhibited by the disassociation
VOL. CXXII. i. b

constants of the fatty acids and by the optical rotations of the acyl-*l*-menthols. When these properties are plotted against the number of carbon atoms in the aliphatic chain, two closely similar curves are obtained showing a kind of double oscillation. When the points corresponding with odd numbers of carbon atoms are joined, a zigzag line is obtained, and the points corresponding with even numbers of carbon atoms lie alternately above and below this line. This type of oscillation appears to be peculiar to the fatty acids and some of their derivatives, and in these series to be confined to dissociation constants and optical rotations. It



is suggested that the phenomenon may be due to the influence of the methyl group on the carboxy-group in, for example, the fatty acid series, when the carbon chain has the form

E. H. R.

The Structure of Carbon Chains. JOHANNES STARK (*Z. anorg. Chem.*, 1921, **119**, 292—298).—An elaboration of the hypothesis put forward by Pauly (preceding abstract) to account for the difference between the physical properties of the odd and even members of an aliphatic homologous series. Generally, when the numerical value of the physical property is plotted against the number of carbon atoms, the points corresponding with the even members of the series fall on one curve and those of the odd members on another, roughly parallel, curve. The difference must be due to a difference in structure of the carbon chain when the number of carbon atoms is even from the structure when the number is odd. The suggestion is made that the difference lies in the curvature of the zigzag chain. A molecule with a straighter chain would be expected to form a more stable space lattice structure than one with a more curved chain, and hence to have a higher melting point. The compounds of the even series have the higher melting points, and it is concluded that these have the straighter chain and the compounds of the odd series the more curved chain. The molecular volumes and boiling points of the two series are consistent with this conclusion.

E. H. R.

Preparation of Aluminium Carbide and of Marsh Gas. O. OHMANN (*Z. physikal. Chem. Unterr.*, 1921, **34**, 76—77).—A mixture of aluminium filings, potassium chlorate, and iron, when ignited in a stream of carbon dioxide, results in the formation of aluminium carbide, Al_4C_3 . When the powder is finely ground and then gently warmed with water, methane is liberated: $\text{Al}_4\text{C}_3 + 6\text{H}_2\text{O} = 3\text{CH}_4 + 2\text{Al}_2\text{O}_3$. Four grams of aluminium yield 70 c.c. of methane.

CHEMICAL ABSTRACTS.

The Formation of Hexachloroethane from Chloropicrin. OSWALD SILBERRAD (*Chem. News*, 1921, **123**, 271).—When hydrogen chloride is passed through chloropicrin at 100° and the resulting mixed vapours are passed over pumice at 400° , the main products are carbonyl chloride, nitroxy chloride, and nitric oxide. A small amount of hexachloroethane is also formed, and may be collected

by passing the cooled gases through a tube lightly packed with asbestos. The asbestos is subsequently extracted with a mixture of alcohol and ether and the hexachloroethane allowed to crystallise out.
W. G.

The Elimination of Hydrogen Chloride from Chlorohydrocarbons. W. F. FARAGHER and F. H. GARNER (*J. Amer. Chem. Soc.*, 1921, **43**, 1715—1724).—The chloro- or dichloro-derivatives of hexane, isohexane, heptane, cyclohexane, and benzene were examined, and the results indicate that they can be classified in the following diminishing order of ease with which hydrogen chloride can be split off: hydroaromatic, aliphatic, aromatic compounds. In the aliphatic compounds the stability of the monochloro-compounds at a given temperature decreases with increasing molecular weight at least up to chlorohexane. Of the three catalysts used, namely, alumina, unglazed porcelain, and unglazed porcelain impregnated with barium chloride, the first named is the most efficient, but all three lose their activity rapidly owing to the poisoning produced by the decomposition of the hydrocarbons. This method of removal of hydrogen chloride is quite satisfactory for the preparation of olefine hydrocarbons, but with diolefines secondary decompositions occur and poor yields are obtained.
W. G.

A Reaction between Methyl Alcohol and Water and some Related Reactions. J. A. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1921, **43**, 1670—1672).—When suitable mixtures of methyl alcohol and water are passed over finely-divided reduced copper at 230—250°, carbon dioxide and hydrogen are produced according to the equation $\text{CH}_3\cdot\text{OH} + \text{H}_2\text{O} = \text{CO}_2 + 3\text{H}_2$. Formaldehyde and water behave similarly.
W. G.

Preparation of Ethyl Alcohol. PAUL PASCAL (Swiss Pat., 8188; from *Chem. Zentr.*, iv, 802—803).—Acetaldehyde is submitted to direct reduction by electrolysis in acid solution. The electrolysis takes place in an apparatus with two chambers separated by a porous diaphragm. The cathode consists of mercury or lead, with or without antimony coating. The anode consists of platinum, lead, ferric oxide, graphite, or carbon. Acetaldehyde is gradually added to the cathode chamber and the electrolysis conducted at a temperature not exceeding 40° and a current density not exceeding 2—3 amperes per square metre. The formation of crotonaldehyde is prevented by shortening the period of reduction. Formation of acetic acid is prevented by the use of the diaphragm and the yield is almost theoretical. In the place of acetaldehyde, its polymericides may be used or acetaldehyde may be formed in the apparatus from acetylene by a catalytic process. The electrolysis may be conducted in the presence of sulphuric acid, phosphoric acid, organic sulphonic acids, or sodium hydrogen sulphate.
G. W. R.

Preparation of β -Chlorohydrins. L. SMITH (*Svensk. Kem. Tidskr.*, 1921, **23**, 75—83).—In an attempt to prepare β -chlorohydrin from glycerol by way of $\alpha\gamma$ -dibromohydrin, β -chloro- $\alpha\gamma$ -

di bromopropene, and β -chloro- α -diacetoxypropene, it was found that the first two reactions proceeded smoothly, but when β -chloro- α -dibromopropene was treated with potassium acetate in a sealed tube at 170° , and the resulting mixture hydrolysed, the product consisted of 70% of α -chlorohydrin and 30% of β -chlorohydrin, the potassium acetate having caused interchange of a chlorine and a bromine atom before the latter was replaced.

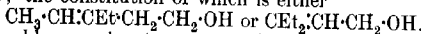
A similar rearrangement was found to occur to a like extent in the attempted preparation of β -chloropropyl alcohol by the action of nitrous acid on β -chloropropylamine. A second method for the preparation of β -chloropropyl alcohol from α -chloro- β -hydroxypropene by way of α -hydroxy- β -benzoyloxypropene, α -bromo- β -benzoyloxypropene, α -phthalimido- β -benzoyloxypropene, and β -chloropropylamine hydrochloride gave a product consisting chiefly of β -chloroisopropyl alcohol. CHEMICAL ABSTRACTS.

New Synthesis of Glycerol and α -Glucoheptol. AMÉ PICOTET and ANDRÉ BARBIER (*Helv. Chim. Acta*, 1921, 4, 924—928).—The synthesis is designed to permit the transformation of a sugar of the C_n series to one of C_{n+1} series and is somewhat allied to Kiliani's method except that the hydrocyanic acid of the latter is replaced by nitromethane, reaction occurring in accordance with the scheme: $R \cdot CHO \rightarrow OH \cdot CHR \cdot CH_2 \cdot NO_2 \rightarrow OH \cdot CHR \cdot CH_2 \cdot NH_2 \rightarrow OH \cdot CHR \cdot CH_2 \cdot OH \rightarrow OH \cdot CHR \cdot CH_2 \cdot OH$. It has been applied successfully to glycolaldehyde and dextrose, but the yields are small; it does not appear to succeed with glycer-aldehyde or *l*-arabinose.

An aqueous solution of glycolaldehyde is heated on a water-bath with the calculated quantity of nitromethane and a little solid potassium hydrogen carbonate. The cooled solution is reduced with aluminium amalgam, the aluminium hydroxide removed, and the base precipitated as the mercurichloride. The latter is decomposed with hydrogen sulphide and the base treated with nitrous acid, whereby glycerol is produced which is isolated in substance and as the tribenzoate. Under similar conditions arabinose is ultimately converted into a substance, colourless needles, m. p. 152° , which does not appear to be a mixture of mannitol and sorbitol, and could not be investigated completely by reason of the small amount available. Glycerol appears to give a normal mercurichloride, but the subsequent treatment of the amine with nitrous acid gives a liquid of boiling point much lower than that of erythritol; it could not be caused to crystallise or converted into a benzoyl or an acetyl derivative. Dextrose is transformed into α -glucoheptol, m. p. 134 — 135° . H. W.

The Condensation Products of Ethyl β -Chloropropionate and Ethyl α -Chloropropionate with Magnesium Ethyl Bromide and some Compounds which are Derived from Them. CHARLES MOUREU and GÉRALD BARRETT (*Bull. Soc. chim.*, 1921, [iv], 29, 993—1006).—Magnesium ethyl bromide reacts

with ethyl β -chloropropionate to give α -chloro- γ -ethylpentan- γ -ol, b. p. $89^\circ/14$ mm.; $d_4^{16.5}$ 1.0164; $d_4^{20.1}$ 1.0108; $n_D^{20.5}$ 1.4579, which is decomposed by potassium hydroxide, giving $\alpha\gamma$ -oxido- γ -ethylpentane, b. p. 129° ; d_4^0 0.8691; $d_4^{19.2}$ 0.8525; n_D^{20} 1.4200 (cf. Maire, A., 1908, i, 247). This oxide, when treated with dry hydrogen chloride, gives γ -chloro- γ -ethylpentan- α -ol, which is very unstable, losing hydrogen chloride on distillation, and gives an unsaturated alcohol, b. p. $79-80^\circ/20$ mm.; d_4^0 0.8822; $d_4^{20.4}$ 0.8658; n_D^{20} 1.4531; the constitution of which is either

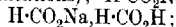


Ethyl α -chloropropionate reacts with magnesium ethyl bromide to give β -chloro- γ -ethylpentan- γ -ol, b. p. $76-76.5^\circ/21$ mm.; d_4^0 1.0124; $d_4^{20.5}$ 1.0073; n_D^{20} 1.4522, which by the action of potassium hydroxide yields $\beta\gamma$ -oxido- γ -ethylpentane, b. p. $125.4-125.8^\circ/760.4$ mm.; d_4^0 0.8496; $d_4^{24.3}$ 0.8275; $d_4^{27.2}$ 0.8245; $d_4^{27.6}$ 0.8241; $n_D^{27.6}$ 1.4063 (cf. Fournneau and Tiffeneau, A., 1907, i, 817). This oxide unites with hydrogen chloride, giving principally the original chlorohydrin.

W. G.

Compound Formation and Solubility in Systems of the Type, Formic Acid : Metal Formate.

JAMES KENDALL and HOWARD ADLER (*J. Amer. Chem. Soc.*, 1921, **43**, 1470-1481; cf. this vol., ii, 33).—The freezing-point curves of the formates of potassium, ammonium, sodium, barium, lithium, calcium, magnesium, zinc, nickel, lead, and copper in formic acid solution, and the acetates of sodium, calcium, zinc, iron (ferrie), and silver in acetic acid solution, have been experimentally determined. In the case of the formates, the following compounds have been isolated: $\text{H}\cdot\text{CO}_2\text{K}\cdot 3\text{H}\cdot\text{CO}_2\text{H}$; $\text{H}\cdot\text{CO}_2\text{K}\cdot 2\text{H}\cdot\text{CO}_2\text{H}$; $\text{H}\cdot\text{CO}_2\text{K}\cdot\text{H}\cdot\text{CO}_2\text{H}$ (m. p. 108.6°); $\text{H}\cdot\text{CO}_2\cdot\text{NH}_4\cdot 3\text{H}\cdot\text{CO}_2\text{H}$; $\text{H}\cdot\text{CO}_2\text{NH}_4\cdot\text{H}\cdot\text{CO}_2\text{H}$ (exists in two crystalline modifications); $\text{H}\cdot\text{CO}_2\text{Na}\cdot 2\text{H}\cdot\text{CO}_2\text{H}$;



and $(\text{H}\cdot\text{CO}_2)_2\text{Ba}\cdot\text{H}\cdot\text{CO}_2\text{H}$; whilst in the case of the acetates only two compounds, $\text{CH}_3\cdot\text{CO}_2\text{Na}\cdot 2\text{CH}_3\cdot\text{CO}_2\text{H}$; and $\text{CH}_3\cdot\text{CO}_2\text{Na}\cdot\text{CH}_3\cdot\text{CO}_2\text{H}$ were isolated. The results of the present work closely resemble those obtained with sulphate systems (A., 1921, ii, 45, 453) in following the general rule previously deduced, that compound formation increases in extent with increasing diversity in the character of the components, the significant variable in systems of the general type $\text{HX}\cdot\text{RX}$ being the position of R relative to H in the $E.M.F.$ series. An examination of the data for sulphates, formates, acetates, fluorides, and hydroxides shows that the rate of decrease in compound formation, in proceeding from more positive radicles (such as potassium) or less positive radicles (such as silver) towards hydrogen, increases the weaker the acid radicle. Solubility and compound formation are again found to proceed in parallel throughout the series. Salts which show extensive compound formation (such as salts of the alkali metals) are also extremely soluble. In passing down the $E.M.F.$ series toward hydrogen, solubility rapidly diminishes and finally becomes inappreciable.

J. P. S.

The Action of Mercurous Formate on certain Aliphatic Halogen Compounds. HERMANN KUNZ-KRAUSE and PAUL MANICKE (*Ber. deut. Pharm. Ges.*, 1921, **31**, 344—349).—Mercurous formate was obtained in small, white, glistening, rhombic prisms by dissolving yellow mercuric oxide in formic acid, and rapidly filtering before reduction of the mercuric formate first formed occurs. Mercurous formate reacts with chloral hydrate and halogen hydrocarbons in a similar manner to mercuric acetate (cf. A., 1921, i, 543), the halogen being eliminated, and carbon dioxide and monoxide evolved, according to the equations: (1) $2\text{CCl}_3\cdot\text{CH}(\text{OH})_2 + 10\text{H}\cdot\text{CO}_2\text{Hg} = 3\text{Hg}_2\text{Cl}_2 + 4\text{Hg} + 6\text{H}\cdot\text{CO}_2\text{H} + 2\text{CO}_2 + 6\text{CO} + 2\text{H}_2\text{O}$; (2) $2\text{CHCl}_3 + 10\text{H}\cdot\text{CO}_2\text{Hg} = 3\text{Hg}_2\text{Cl}_2 + 4\text{Hg} + 6\text{H}\cdot\text{CO}_2\text{H} + 2\text{CO}_2 + 4\text{CO}$.
G. F. M.

Catalytic Effect of Ammonia on the Oxidation of Butyric Acid with Hydrogen Peroxide. EDGAR J. WITZEMANN (*J. Biol. Chem.*, 1921, **49**, 123—141).—In his oxidation experiments with hydrogen peroxide, Dakin (A., 1908, i, 74, 119) used the ammonium salts of fatty acids. The author could not repeat Dakin's experiments when using potassium hydroxide (A., 1918, i, 422). He now finds that ammonia acts as a catalyst, up to four equivalents. One equivalent of ammonium or potassium hydroxide is more efficient than two equivalents of either. It is suggested that the ammonia effect may be the agency by which the normal oxidation of fatty acids is brought about by the liver. As in Dakin's experiments, the oxidation took place at the β -carbon atom, acetone being formed.
G. B.

α -Hydroxy-lactones. BURCKHARDT HELFERICH and JOHANN ADOLF SPEIDEL (*Ber.*, 1921, **54**, [B], 2634—2640).—The investigation was undertaken with the object of examining the possibility of the reduction of α -hydroxy-lactones by sodium amalgam in faintly acid solution to α - γ -dihydroxy-aldehydes. Under these conditions, α -hydroxy- γ -valerolactone and α -hydroxy- γ -hexolactone yield substances with aldehydic properties, but, in each case, the amount of available material was insufficient for an extended examination.

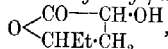
Crystalline chloroparacetaldehyde is obtained conveniently by the distillation of chloroacetal with anhydrous oxalic acid and cautious treatment of the distillate after it has been preserved during three to four days with half its volume of concentrated sulphuric acid at 0°. (Crystalline bromoparacetaldehyde, long, colourless needles, is prepared similarly from bromoacetal; when slowly distilled in an atmosphere of carbon dioxide, it gives a colourless liquid of indefinite boiling point which gradually passes into a solid modification distinct from the original compound.) Chloroparacetaldehyde is transformed by an ethereal solution of magnesium ethyl bromide into α -chloro- β -hydroxybutane, a colourless liquid which rapidly darkens when preserved, b. p. 52°/15 mm., d_4^{20} 1.040, n_D^{20} 1.4353. The latter is converted by a solution of ethyl sodium malonate in absolute alcohol at the atmospheric temperature into

α -carbethoxy- γ -hexolactone, $\text{O} \begin{array}{c} \text{CO}-\text{CH}-\text{CO}_2\text{Et} \\ | \\ \text{CHEt}-\text{CH}_2 \end{array}$, a viscous liquid,

b. p. $144^\circ/8$ mm., d_4^{20} 1.1119, n_D^{20} 1.4463, which is transformed by bromine in chloroform solution into α -bromo- α -carbethoxy- γ -hexo-

lactone, $\text{O} \begin{array}{c} \text{CO}-\text{CBr}-\text{CO}_2\text{Et} \\ | \\ \text{CHEt}-\text{CH}_2 \end{array}$, a heavy, yellow liquid, b. p. $148^\circ/5$

mm., d_4^{20} 1.427, n_D^{20} 1.4767. The bromo-derivative is transformed by hydrobromic acid (d 1.49) and subsequent heating of the product at 120 – 150° into (?) bromohexolactone, $\text{C}_6\text{H}_9\text{O}_2\text{Br}$, b. p. $142^\circ/18$ mm., d_4^{20} 1.4826, n_D^{20} 1.4841. α -Hydroxy- γ -hexolactone,



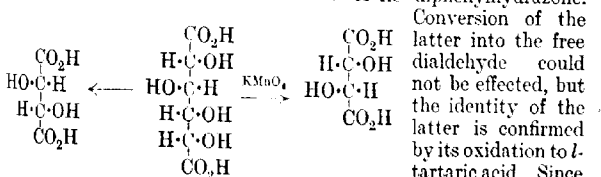
b. p. $127^\circ/5$ mm., d_4^{24} 1.1454, n_D^{24} 1.4517, is prepared by the hydrolysis of the bromo-ester with potassium hydroxide solution and elimination of carbon dioxide from the product by distilling it under diminished pressure. By performing the hydrolysis with barium hydroxide, it is possible to isolate the intermediately-formed β -hydroxybutylhydroxymalonic acid, $\text{OH}\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{C}(\text{CO}_2\text{H})_2\cdot\text{OH}$, a viscous, pale red liquid and its barium salt. The hydroxy-lactone is converted by boiling aqueous barium hydroxide solution into barium $\alpha\gamma$ -dihydroxy- n -hexoate, an amorphous, hygroscopic solid.

H. W.

**The Conditions Underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. III. Products Derived from Halogenated Glut-
aconic Acids.** ERNEST HAROLD FARMER and CHRISTOPHER KELK
INGOLD (T., 1921, 119, 2001–2021).

The Reversibility of the Michael Reaction. CHRISTOPHER
KELK INGOLD and WALTER JAMES POWELL (T., 1921, 119, 1976–
1982).

Degradation of d -Saccharic Acid to the Dialdehyde of l -Tartaric Acid. MAX BERGMANN (*Ber.*, 1921, 54, [B], 2651–
2658).—The action of bromine and potassium hydroxide on the
diamide of saccharic acid leads to the formation of l -tartardialde-
hyde, which is isolated in the form of its diphenylhydrazone.



that d -tartaric acid is formed by the oxidation of d -saccharic
acid with potassium permanganate, an example is given of the
production of enantiomorphous forms by the action of different
reagents on the same compound owing to removal of different
portions of the original molecule as shown by the annexed scheme.

The diamide of *d*-saccharic acid, hexagonal plates, decomp. 170° when rapidly heated, is obtained readily and in excellent yield by the action of concentrated ammonia on free saccharic acid which has been dehydrated at 100° in a vacuum (and hence, presumably, has been converted into the corresponding dilactone). It is oxidised by bromine in the presence of potassium hydroxide to *l*-tartardialdehyde, which is converted by immediate addition of phenylhydrazine into a mixture of *l*-tartardialdehyde- α -diphenylhydrazine, almost colourless, 3- to 6-sided leaflets or microscopic needles, decomp. 177 – 179° after darkening above 160° , $[\alpha]_D^{20} -99.6^{\circ}$ in pyridine solution (the substance is probably not quite homogeneous) and *l*-tartardialdehyde- β -diphenylhydrazine, almost colourless crystals, decomp. 195° after darkening above 170° , $[\alpha]_D^{20} -1^{\circ}$ to -2° in pyridine solution. The α -diphenylhydrazine is converted by benzaldehyde in aqueous alcoholic solution into *l*-tartardialdehydemonophenylhydrazine; individual specimens of the latter which appear to be analytically pure show widely-varying melting points, whereas the specific rotation is practically constant ($[\alpha]_D^{20} -182.7^{\circ}$ in alcoholic [50%] solution). The oxidation to *l*-tartaric acid is effected by treatment of the diphenylhydrazine with benzaldehyde as just described, removal of the monophenylhydrazine, and treatment of the filtrates from the latter with bromine at 50° . *l*-Tartardialdehydemonophenylhydrazine is converted by a dilute solution of hydrogen chloride in absolute methyl alcohol at 20° into the base, $C_{10}H_9ON_2$, which is presumably a pyridazine derivative; it crystallises in lustrous, hexagonal plates, decomp. 160 – 170° , according to the rate of heating. The corresponding *hydrochloride*, plates or slender needles, decomp. about 213° , the *nitrate*, plates (+ H_2O), the *picrate*, canary-yellow prisms, and the unstable *nitrite* are described.

H. W.

A New Preparation of Formaldehyde Hyposulphite and an Economical Generator of Hyposulphurous Acid. PH. MALVEZIN, CH. RIVALLAND, and L. GRANDCHAMP (*Compt. rend.*, 1921, 173, 1180–1182).—When zinc dust is suspended in a 40% solution of formaldehyde and sulphur dioxide is passed into the solution through the walls of a Chamberland filter, a concentrated solution of zinc-formaldehyde hyposulphite is obtained and the salt crystallises out on cooling. This material is a very powerful reducing agent for dyes such as indigotin, and is much more economical for use in the industry than the 88–90% hyposulphite. W. G.

The Action of Hydrogen Phosphide on Formaldehyde. ALFRED HOFFMAN (*J. Amer. Chem. Soc.*, 1921, 43, 1684–1688).—When hydrogen phosphide is passed into a warm aqueous solution of formaldehyde acidified with hydrochloric acid, *tetramethylol-phosphonium chloride*, $PCl(CH_2OH)_4$, m. p. 151° , is obtained. When acted on by alkali hydroxides or carbonates, it yields a syrupy compound, $C_3H_9O_3P$, which gives a *tribenzoyl* derivative, m. p. 111° . When calcium carbonate is added to an aqueous solution of the phosphonium chloride, carbon dioxide is evolved,

and if the mixture is warmed, hydrogen and formaldehyde pass off and the syrupy compound described above is obtained. When ammonia is passed into a solution of the phosphonium chloride in methyl alcohol, a compound is obtained in the form of a curdy, white precipitate, but its constitution has not been determined.

W. G.

γ -Hydroxyaldehydes. IV. γ -Hydroxyaldehydes with Tertiary Hydroxyl. BURCKHARDT HELFERICH and MAX GEHRKE (*Ber.*, 1921, 54, [B], 2640—2647; cf. A., 1921, i, 421).—The substances of the types, $\text{CHO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CRMe} \cdot \text{OH}$, or $\text{O} < \begin{smallmatrix} \text{CH}(\text{OH}) \cdot \text{CH}_2 \\ \text{CRMe} - \text{CH}_2 \end{smallmatrix}$

are prepared by the action of suitable Grignard's reagents on methylheptenol, fission of the primary products with ozone, and reduction of the ozonides. The ethyl, *n*-propyl, phenyl, and benzyl compounds are described. The new aldehydes, like those with the secondary hydroxyl group described previously, appear to be exclusively or mainly cyclic in structure, since they react gradually with magenta-sulphurous acid solution or ammoniacal silver and give methyl semiacetals with methyl alcoholic hydrogen chloride which are hydrolysed by dilute acids, but not by emulsin. They lose water more readily than do the corresponding compounds with a secondary alcoholic group, passing thereby into dihydrofuran derivatives.

γ -Hydroxy- γ -methyl-*n*-hexaldehyde, $\text{CHO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMeEt} \cdot \text{OH}$, or 5-hydroxy-2-methyl-2-ethyltetrahydrofuran, $\text{O} < \begin{smallmatrix} \text{CH}(\text{OH}) \cdot \text{CH}_2 \\ \text{CMeEt} - \text{CH}_2 \end{smallmatrix}$ is a colourless, mobile liquid, b. p. 77—82°/10 mm., d_4^{20} 0.9742, n_D^{20} 1.4411. The corresponding methyl semiacetal, $\text{O} < \begin{smallmatrix} \text{CH}(\text{OMe}) \cdot \text{CH}_2 \\ \text{CMeEt} - \text{CH}_2 \end{smallmatrix}$,

a colourless liquid, has b. p. 61.5°/32 mm., d_4^{20} 0.9106, n_D^{20} 1.4218. β -Propylmethylheptenol, $\text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMePr} \cdot \text{OH}$, b. p. 112—113°/10 mm., d_4^{20} 0.8445, n_D^{20} 1.4500, is converted in the usual manner into γ -hydroxy- γ -methylheptaldehyde (or 5-hydroxy-2-methyl-2-propyltetrahydrofuran, b. p. 94—95°/12 mm., d_4^{20} 0.9661, n_D^{20} 1.4400, from which 5-methoxy-2-methyl-2-propyltetrahydrofuran, b. p. 58—60°/10 mm., d_4^{20} 0.8990, n_D^{20} 1.4238, is obtained. β -Phenylmethylheptenol, b. p. 107—109°/2 mm., d_4^{20} 0.9680, n_D^{20} 1.5205, is transformed into γ -hydroxy- γ -phenylvaleraldehyde, b. p. 123—124°/2 mm. (slight loss of water occurs during distillation even at this pressure), d_4^{20} 1.016, n_D^{20} 1.5382, which yields 5-methoxy-2-phenyl-2-methyltetrahydrofuran, a colourless liquid, b. p. 128°/16 mm., d_4^{20} 1.033, n_D^{20} 1.5288. β -Benzylmethylheptenol, an almost colourless, viscous liquid, b. p. 127—129°/3 mm., d_4^{20} 0.9550, n_D^{20} 1.5161, is converted into the corresponding aldehyde in a similar manner, but the latter cannot be purified by distillation on account of the readiness with which it loses water and passes into 2-benzyl-2-methyl-2:3-dihydrofuran, $\text{O} < \begin{smallmatrix} \text{CH} = \text{CH} \\ \text{CMe}(\text{CH}_2\text{Ph}) - \text{CH}_2 \end{smallmatrix}$ a pale yellow liquid, b. p. 118°/2.8 mm., d_4^{20} 1.042, n_D^{20} 1.5329. The undistilled

b*

aldehyde is readily convertible into 5-methoxy-2-benzyl-2-methyltetrahydrofuran, a colourless, viscous liquid, b. p. 133—135°/3.5 mm., d_4^{20} 1.020, n_D^{20} 1.5124. The dihydrofuran derivative unites with bromine in chloroform solution, but removal of the solvent is accompanied by loss of hydrogen bromide and formation of 4(?)-bromo-2-benzyl-2-methyl-2:3(?)-dihydrofuran, $C_{12}H_{13}OBr$, short, colourless prisms, b. p. 140—141°/2.8 mm. H. W.

Synthesis of Sugars from Formaldehyde, Carbon Dioxide, and Water. A. J. EWART (*Proc. Roy. Soc. Victoria*, 1919, **31**, 378—387; cf. *ibid.*, 1918, **30**, 178—209).—The main conditions for the polymerisation of formaldehyde to sugar by alkali hydroxides and carbonates are appropriate dilution and a temperature of 100° to 110°; the most rapid reaction is produced by sodium hydroxide, particularly in the presence of a neutral calcium salt. The by-products are mainly formates and methyl alcohol. The sugar obtained is optically inactive, and contains reducing pentoses and reducing fermentable hexoses. Carbon dioxide and water are readily polymerised to sugar by the aid of magnesium. The production, previously noted, of calcium tartrate during the synthesis of sugar, was not confirmed. CHEMICAL ABSTRACTS.

Starch. J. J. LIJST ZWIKKER (*Rec. trav. chim.*, 1921, **40**, 605—615).—An investigation of the colloidal condition of grains of four kinds of starch shows that the degree of dispersion is different in each case. Solutions, prepared in the cold from grains which had been mechanically broken up, were submitted to ultrafiltration and the amylose content of the ultra-filtrates was determined. Solutions prepared by heating gave no amylose in the ultra-filtrate. The colloidal condition of amylopectin differs from that of amylose. Amylophosphoric acid derives its character from amylopectin by reason of the nature of the kations which are present; these also have a marked influence on the adsorption power of the starch.

Adsorption experiments are discussed and the conclusion is drawn that starch is more closely allied to cellulose than has hitherto been supposed. H. J. E.

Constitution of Starch Iodide. A. LOTTERMOSER and MAX STREUDE (*Z. Elektrochem.*, 1921, **27**, 496—501; cf. *A.*, 1921, i, 708).—An attempt is made to elucidate the constitution of starch iodide from measurements of *E.M.F.* The potential of the element $Pt|I_2|I^-$ has been measured with changing iodine concentration and constant iodide concentration in aqueous solutions. The potassium iodide concentrations used were 0.1*N*, 0.2*N*, and 0.01*N*, and the amount of free iodine added varied from 0.00019 to 0.585 millimols.; all measurements were made at 25°. It is shown that the logarithm of the total iodine concentration varies in an almost linear manner with the potential. Hence knowing the inclination of the curve for a given concentration of potassium iodide, it becomes possible to determine from the curves the total iodine concentration. The curve constants *a* and *b* were determined for each concentration of potassium iodide by the equation $e_h = a + b \log c$, and the

values found were 0.1*N*-potassium iodide $a=0.544$, $b=0.0310$, 0.2*N*-potassium iodide, $a=0.518$, $b=0.0313$, and 0.01*N*-potassium iodide, $a=0.634$, $b=0.0342$. Solutions of potassium iodide in 0.1% soluble starch to which steadily increasing amounts of iodine were added were then measured, and from the potential and the curves the logarithm of the iodine concentration in the water phase was obtained. Thus the quantity of iodine taken up by the starch can be calculated. A number of experiments on the partition of iodine between water and carbon tetrachloride in the presence of starch are described.

J. F. S.

Polysaccharides. XII. Glycogen. P. KARRER (*Helv. Chim. Acta*, 1921, 4, 994—1000).—Glycogen differs from starch mainly in its inability to swell in water and in giving a reddish-brown coloration with iodine. The chemical similarity of the substances is further exemplified by the conversion of glycogen by methyl sulphate and barium or sodium hydroxide into *methylglycogen*, $[\alpha]_D -206^\circ$ in aqueous solution, the properties of which agree even in detail with those of methylstarch. Similarly, glycogen is transformed by sodium hydroxide into a compound, $(C_{12}H_{20}O_{10}.NaOH)_x$, which therefore has the same composition as the similar substance obtained from starch.

The hypothesis has been advanced previously that glycogen is differentiated from starch chiefly by the degree or mode of polymerisation of the maltose anhydride, although the heats of combustion of the substances show that the difference in the degree of polymerisation cannot be very great. On the other hand, it is possible that starch and glycogen are fundamentally identical, and that their differing behaviour towards iodine and water are caused by the presence of impurities. The formation of coloured adsorption compounds with iodine is characteristic of the colloidal condition and is greatly dependent on the size of the particles and other external factors. The relationship between starch and glycogen is very similar to that between amylose and amylopectin; in the latter case, it is highly probable that the difference is due to the presence of a small amount of a compound of phosphorus.

H. W.

Action of Ferments on Laminarin. (MME) Z. GRUZEWSKA (*Bull. Soc. Chim. Biol.*, 1921, 3, 490—497).—Although laminarin (cf. Kylin, A., 1915, i, 931) can be utilised by the animal organism, experiments *in vitro* indicate that pancreatic juice, gastric juice, and invertase of animal origin are without action on it. Diastase and invertase from vegetable sources, however, ferment it slowly, whilst hydrochloric acid hydrolyses it completely, the product in each case being dextrose. Of the ferments tested, that obtained from snails (*Helix pomatia*) was found to be most active. E. S.

Comparative Action of Heat on Cellulose, Hydrocellulose, and Oxycellulose and the Characterisation of Hydrocellulose by Dry Heat. ED. JUSTIN-MUELLER (*Bull. Soc. chim.*, 1921, [iv], 29, 987—988).—Hydrocellulose caramelises at a lower temperature than oxycellulose and at a much lower temperature

than cellulose. If the specimen under examination is submitted to dry heat, it will assume a brown colour at 130–150°, at which temperature oxycellulose shows at most only a pale yellow colour and cellulose no change at all.

W. G.

Cellulose. V. A New Degradation of Cellulose. Conversion of Cellulose into a Biose Anhydride. KURT HESS (*Ber.*, 1921, 54, [B], 2867–2885).—Previous methods of fission of cellulose have led to the recognition of cellobiose and dextrose as important products, but they do not permit a decision as to whether cellobiose is the fundamental unit in the structure of the cellulose molecule and dextrose is formed therefrom or whether dextrose itself is also an essential factor in the formation of cellulose (cf. A., 1921, i, 710). Various new methods of degrading cellulose have therefore been investigated.

When treated with ethyl alcohol and hydrogen chloride, cellulose yields indefinite, dark-coloured products which do not reduce Fehling's solution and have a small ethoxyl content. A mixture of glacial acetic acid and hydrogen bromide also gives unsatisfactory results. The use of acyl haloids, however, is more promising and the action of acetyl chloride, acetyl bromide, benzoyl bromide, thionyl chloride, and propionyl bromide and absolute hydrogen haloids on cotton cellulose, wood cellulose, acetylcellulose, and ethylcellulose has been investigated. With acetyl chloride, complete solution of the cellulose results within four to five days, whilst with acetyl bromide the process is even more rapid. Benzoyl bromide attacks cellulose without dissolving it. Propionyl bromide causes solution. On the other hand, thionyl chloride appears to have no action on the fibre; a proof is thus afforded that the action observed with other acyl haloids is not entirely due, at any rate, to the liberated halogen acid, but that the acyl haloid must itself play an important rôle.

Cellulose is converted by acetyl bromide into a yellow syrup containing bromine, only part of which can be exchanged for hydroxyl by means of silver carbonate and moist acetone. After acetylation of the crude product with pyridine and acetic anhydride, about one-third of it is obtained in the form of penta-acetyl- β -glucose. The remaining, non-crystalline product contains about 13% of bromine and, as judged from determinations of its molecular weight, contains, in part, a biose derivative. Cellobiose is also converted by acetyl bromide into penta-acetylglucose and sugars containing bromine. Under similar conditions, maltose appears to be transformed into acetylbromomaltose, which is subsequently decomposed into acetylbromoglucose and small amounts of an acetylbromoglucose bromohydrin of doubtful constitution. [This observation throws some doubt on Karrer's claim of the quantitative conversion of amylose into acetylbromomaltose (cf. A., 1921, i, 311).] Ethylcellulose and acetyl bromide similarly yield a brominated product from which it has been found possible to isolate a crystalline bromoacetyl ethylglucose, m. p. 123°, which is to be more fully described in a subsequent communication.

The action of acetyl chloride proceeds in a totally different manner, an almost colourless solution being obtained which solidifies rapidly when concentrated. The product is separable by solution in glacial acetic acid and precipitation with ether into an insoluble and a soluble portion; the latter, which can be caused to solidify by evaporation of the solution, dissolving the residue in chloroform, and precipitation by ether, has not yet been examined completely. The former consists of a mixture of a hexa-acetylanhydrobiose and a chloropenta-acetylanhydrobiose, the relative proportions of which depend on the duration of the original action. By treatment with acetic anhydride and sodium acetate, this product is converted into an apparently homogeneous *hexa-acetylanhydrobiose*, $C_{24}H_{32}O_{16}$, small, colourless crystals, m. p. $265-270^{\circ}$, $[\alpha]_D^{25} = -17.8^{\circ}$, in chloroform solution. The substance has a pronounced tendency to yield colloidal solutions: Dilute solutions of it in glacial acetic acid have a molecular weight corresponding closely with the value calculated from the formula given above, but marked association is observed in more concentrated solutions. In phenol, the substance is bimolecular, whereas in bromoform the association is complete and a depression of the freezing point is not observed. In its general properties, therefore, the new substance exhibits a close analogy with cellulose and its esters. Treatment with alcoholic potassium hydroxide solution at the atmospheric temperature converts the hexa-acetate into the corresponding *anhydrobiose*, $C_{12}H_{20}O_{10} \cdot 2H_2O$, an apparently microcrystalline powder which becomes discoloured at 200° , but is not melted completely at 270° . It is insoluble in water, but soluble in ammoniacal copper hydroxide solution. It is soluble in cold alkali hydroxide and is precipitated unchanged from such solutions by acids; with warm solutions, this is not the case. The solubility in ammoniacal copper hydroxide solution does not depend, however, on the basic character of the latter, since a similar solvent action is exerted by ammoniacal silver oxide, but not by ammoniacal cadmium hydroxide solution. The substance shows distinct adsorptive capacity for substantive cotton dyes.

H. W.

Cellulose Nitrates. G. DE BRUIN (*Rec. trav. chim.*, 1921, **40**, 632-664).—A résumé is given of the more generally accepted views as to the constitution of cellulose from the point of view of its nitration products and also of the various methods of determining its stability and the ratio of nitrogen content to stability. For the work described, a large quantity of material was used and details are given with regard to the cellulose, acids, nitration, stabilisation, and method of sampling and of carrying out estimations of nitrogen content. The relation between stability and nitrogen content at 95° and 132° is expressed both numerically and graphically, the author's method of investigation being described in detail. This is followed by a review of work carried out on the solubility of cellulose nitrates in mixtures of alcohol and ether, together with methods of experiment hitherto in use. The author's results as regards solubility, expressed as the mean of a series

of determinations of the ratio of solubility to nitrogen content vary considerably with methods of preparation of the cellulose nitrate. The author infers from his experimental work on stability and solubility that there are simple cellulose nitrates the nitrogen content of which is about 12% and 12.5% respectively; it is shown that the substance containing 12.75% of nitrogen is present as a mixture of two isomerides one of which is soluble in a mixture of alcohol and ether, the other being insoluble. These results are in accordance with the theory put forward by Vieille. H. J. E.

Lignosulphonic Acid. PETER KLASON (*Zellstoff u. Papier*, 1921, 1, 56).—The author criticises the formula proposed for the barium salt of lignosulphonic acid by Hönig and Fuchs (*A.*, 1920, i, 753) and proposes $C_{18}H_{18}O_{11}S_2Ba$ in place of the formula $C_{18}H_{30}O_{10}S_2Ba$. * CHEMICAL ABSTRACTS.

Action of Ozone on Aliphatic and Aromatic Substitution Products of Ammonia. WILHELM STRECKER and MAX BALTES (*Ber.*, 1921, 54, [B], 2693—2708; cf. Strecker and Thienemann, *A.*, 1921, ii, 44).—The action of ozone on substitution products of ammonia only leads to oxidation with addition of oxygen when the radicles attached to the nitrogen atom are similar to one another and of not too great molecular weight; thus, the tertiary aliphatic amines give the corresponding amine-oxides, whereas triphenylamine gives at the most a highly unstable product. If the substituents differ from one another, as is the case with the primary and secondary aliphatic amines and the *N*-alkylanilines, ozonisation causes the degradation of the molecule. With aromatic derivatives, ozonisation does not cause an extensive change in the molecule when the oxidation product is a particularly stable substance.

Undiluted trimethylamine reacts explosively with ozone. In chloroform solution at -80° , the base is converted into a mixture of trimethylamine *N*-oxide and its hydrochloride (cf. Dunstan and Goulding, *T.*, 1899, 75, 792, 1005), the requisite hydrogen chloride being derived from a partial oxidation of the solvent. A precisely similar reaction is observed in carbon tetrachloride solution at -30° . In aqueous solution, trimethylamine oxide is likewise produced in small amount, but, in this instance, its formation is accompanied by the production of formaldehyde. Ozonisation in the presence of much hexane gives formaldehyde and a viscous, white mass which melts to a yellow oil, insoluble in hexane, when removed from the cooling bath. The oil soon decomposes with evolution of nitrogen, hydrogen, and formaldehyde; on distillation, it yields carbon dioxide, formaldehyde, and monomethylamine. When treated with hydrogen chloride either before or after the spontaneous evolution of gas, it gives small amounts of trimethylamine oxide hydrochloride. Formaldehyde and dimethylamine are obtained when its aqueous solution is evaporated with hydrochloric acid. It appears probable that an aldim or a substance such as trimethyltrimethyleamine is intermediately formed.

Ozonisation in ethyl chloride solution proceeds in much the same manner as in hexane, except in so far as small amounts of trimethylamine oxide hydrochloride are formed.

Triethylamine is less vigorously attacked than trimethylamine by ozone, but the processes are otherwise similar. In chloroform solution, triethylamine oxide hydrochloride together with small amounts of diethylamine hydrochloride are produced. In hexane, a pale yellow oil is formed which contains diethylamine and acetaldehyde, from which gas is not evolved. A similar effect is observed in ethyl chloride, but, in this case, triethylamine oxide hydrochloride is also produced in small quantity.

Tri-*n*-propylamine when dissolved in chloroform gives tripropylamine oxide hydrochloride (identified as the picrate, m. p. 129.5°). In the absence of solvent, the amine oxide is also formed, but the oxidation proceeds farther with production of aldehyde and nitrate.

Dimethylaniline could not be converted into its oxide by means of ozone, the main products being formaldehyde and more or less resinous substances. Diphenylamine and tetraphenylhydrazine did not give characteristic products when ozonised. Triphenylamine yielded a flocculent precipitate which decomposed with evolution of gas when filtered; possibly an unstable amine oxide is formed. In substance or in solution, phenylhydrazine is decomposed extensively by ozone, with the production of a black mass resembling pitch. Phenylhydroxylamine, on the other hand, is transformed into nitrobenzene in fairly good yield, whilst hydrazobenzene is converted smoothly into azobenzene. Tribenzylamine is oxidised to benzoic acid, small amounts of benzaldehyde being also produced.

H. W.

Ammonium Radicles. II. Tetraethylammonium. II.
HANS HEINRICH SCHLUBACH and FRITZ BALLAUF (*Ber.*, 1921, **54**, [B], 2811–2825).—An extension of previous work (Schlubach, A., 1920, i, 822).

A solution of tetraethylammonium iodide in liquid ammonia at -70° is subjected to electrolysis in a specially designed cell which is fully described and figured in the original. The phenomena are very similar to those observed with tetraethylammonium chloride, blue streaks appearing immediately at the cathode and a dark blue solution being formed. The latter is decolorised immediately by iodine, with formation of tetraethylammonium iodide and reacts with sulphur with apparent formation of *tetraethylammonium sulphide*, $(\text{NEt}_4)_2\text{S}$. When a slow current of dry oxygen is passed over the cathode, the blue solution becomes slowly decolorised, but the phenomenon is not caused by union of the radicle with the gas (see later), and a substance analogous to potassium peroxide does not appear to be formed. With 2:6-dimethyl- γ -pyrone, an immediate change in colour from blue to yellow is observed, and the solution, when evaporated, leaves a red substance analogous to Schlenk and Thal's potassium-dimethylpyrone (A., 1913, i, 1205); the product is stable in an atmosphere of nitrogen at the atmospheric temperature, but rapidly

becomes smeary when exposed to air. Similarly, benzophenone gives a pale violet compound. Attempts to prepare triphenylmethyltetraethylammonium, either from its components in liquid ammonia or by the simultaneous electrolysis of tetraethylammonium chloride and triphenylmethyl chloride, did not lead to the desired result.

The observation that the amount of tetraethylammonium iodide produced does not vary greatly with the intensity of the blue colour of the solution of the radicle has led to the discovery that the solutions gradually become colourless when preserved at a low temperature, but retain their ability to react with iodine, sulphur, and 2:6-dimethyl- γ -pyrone in the same manner as do the blue solutions. The blue radicle, therefore, becomes transformed into a colourless variety. The same modification is produced when a slight excess of tetraethylammonium chloride is allowed to remain for twenty to twenty-four hours in contact with a solution of potassium in liquid ammonia at -70° . The latter method of preparing the radicle is preferable to the electrolytic process, since it permits the use of larger quantities of material and also avoids the decomposition of the product by the heat liberated by the current. The colourless form of tetraethylammonium is unstable at the temperature of boiling ammonia, since it is decomposed completely when its solutions are evaporated. The change does not appear to occur in the same manner as with the blue variety, since the volume of gas evolved is greatly in excess of that required by the equation $2\text{NEt}_4 \rightarrow 2\text{NEt}_3 + \text{C}_4\text{H}_{10}$ (cf. Schlubach, *loc. cit.*).

The relationship between the blue and colourless varieties has not been elucidated completely, but it is suggested that a case of association is presented, 2NEt_4 (blue) \rightleftharpoons $\text{NEt}_4 \cdot \text{NEt}_4$ (colourless); the phenomena are thus comparable with those observed with triarylmethyls and hexa-arylethanes and with diarylnitrogens and tetra-arylhydrazines.

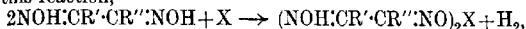
H. W.

Bromo-salts of Ruthenium [Ruthenibromides]. A. GUTHRIE and F. KRAUSS (*Ber.*, 1921, **54**, [B], 2835—2838).—In continuation of previous work on ruthenichlorides (A., 1915, i, 120), a series of the corresponding bromo-salts is described.

The following pentabromo-compounds were prepared by mixing suitably concentrated solutions of their components. They are readily decomposed in aqueous or aqueous-alcoholic solution, particularly when warmed. They can be crystallised from moderately dilute hydrobromic acid, from which they separate in lustrous, dark-coloured crystals which are stable towards air. *Methylammonium ruthenipentabromide*, $(\text{NH}_2\text{Me})_2\text{RuBr}_5$, needles; *dimethylammonium*, $(\text{NH}_2\text{Me}_2)_2\text{RuBr}_5$, needles; *trimethylammonium*; *tetraethylammonium*, leaflets; *ethylammonium*, needles; *diethylammonium*, needles; *triethylammonium*, thick plates; *tetraethylammonium*, leaflets; *n-propylammonium*, needles; *isopropylammonium*, needles; *dipropylammonium*; *n-butylammonium*, small needles; *isobutylammonium*; *isoamylammonium*, needles; *pyridinium*, scales; β -*picolinium*, $(\text{C}_6\text{H}_4\text{Me}\cdot\text{NH})_2\text{RuBr}_5$; *quinolinium*, needles.

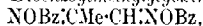
The solutions of the pentabromides in hydrobromic acid instantly react with bromine vapour at the atmospheric temperature, giving the hexabromides, which separate in sparingly soluble, dark coloured crystals. The following new compounds are described; *dipropylammonium ruthenihexabromide*, $(\text{NH}_2\text{Pr}_2)_2\text{RuBr}_6$, long needles; *isoamylammonium*; *β -picolinium*, needles; *quinolinium*. H. W.

Dioximes. GIACOMO PONZIO (*Gazzetta*, 1921, **51**, ii, 213—28; *Atti Accad. Sci. Torino*, 1921, **56**, 90—106).—In hot aqueous solution, the *syn*-modifications of dioximes of α -keto-aldehydes and α -diketones react directly with iron, copper, nickel, and cobalt in compact strips, giving the corresponding internal complex salts. In this reaction,



which possibly occurs also with other elements of Group VIII in the periodic system, the *syn*-glyoximes resemble strong acids, although they are not electrolytes and attack neither magnesium nor zinc. In this way, cobalt, copper, and iron mostly yield either deep brown colloidal solutions or amorphous precipitates, but cupric dimethylglyoxime has been obtained crystalline.

Methylglyoxime, prepared by way of oximinoacetone, exhibits normal cryoscopic behaviour in water, has the molecular electrical conductivity Λ_{32} 0.062, and dissolves in water to the extent of approximately 2.08% at 8°, 4.58% at 26°, and 7.56% at 40°. Nickel methylglyoxime (Tschugaev, A., 1911, i, 261) crystallises in bright red prisms, begins to turn brown at about 200° without melting, dissolves in water to the extent of 0.0131% at 16° and 0.0396% at 100°, yields a scarlet precipitate of nickel dimethylglyoxime when treated in aqueous solution with dimethylglyoxime and a drop of ammonia solution, and dissolves in sodium hydroxide solution, giving an orange-yellow liquid which gradually deposits nickelous hydroxide. *Dibenzoylmethylglyoxime*,



crystallises in white needles, m. p. 164—165°.

Two methods are given for the preparation of dimethylglyoxime, both making use of oximinomethyl ethyl ketone, which is prepared in the one case from methyl acetoacetate and in the other from methyl ethyl ketone. When crystallised from toluene, dimethylglyoxime has m. p. 240° (partial sublimation), and its solubility in water varies from 0.32 gram per litre at 0° to 5.66 grams at 100° and is represented by the expression, $\log S = 1.50515 + 0.015251t - 0.000027725t^2$. Its copper compound, contrary to Tschugaev's statement (A., 1905, i, 743), is insoluble in the ordinary organic solvents with the exception of alcohol. The *cobaltous* salt, $(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2\text{Co}$, obtained by heating either the aqueous solution of the glyoxime with a strip of copper or the alcoholic solution with aqueous cobalt acetate, forms a coffee-coloured powder with violet reflexion and commences to undergo change at about 200°. The dibenzoyl derivative has m. p. 225° (cf. Diels and Stern, A., 1907, i, 480).

Methylethylglyoxime, $\text{NOH}\cdot\text{CMe}\cdot\text{CEt}\cdot\text{NOH}$, crystallises in white

needles or laminae, m. p. 172—173°, and its solubility in water is expressed by the equation $\log S = 1.81837 + 0.02317t - 0.00009015t^2$. The compound described in Richter's *Lexikon* (I, 290) as $\alpha\beta$ -dioxymiminopentane, $\text{NOH}\cdot\text{CH}\cdot\text{CPr}\cdot\text{NOH}$, m. p. 168°, does not exist. *Dibenzoylmethylethylglyoxime*, $\text{C}_{19}\text{H}_{18}\text{O}_4\text{N}_2$, crystallises in long, white, lustrous plates, m. p. 173°.

Methyl-*n*-propylglyoxime crystallises in large, lustrous plates or long, flattened needles, m. p. 175°, and its solubility in water is given by the expression,

$$\log S = 1.23045 + 0.00478637t + 0.0001350812t^2.$$

The nickel salt forms orange needles, m. p. 159—160°, and the same melting point is found for the compound prepared by Tschugaev's method (*loc. cit.*), although this author gave m. p. 144°. The *dibenzoyl* derivative, $\text{C}_{20}\text{H}_{20}\text{O}_4\text{N}_2$, crystallises in white needles, m. p. 128°.

Methylisopropylglyoxime, $\text{C}_6\text{H}_{12}\text{O}_2\text{N}_2$, crystallises in lustrous laminae or long, slender needles, m. p. 157—158°, and its solubility in water is expressed by

$$\log S = 0.23044 - 0.00075979t + 0.00015876t^2.$$

The *nickel* compound, $(\text{C}_6\text{H}_{11}\text{O}_2\text{N}_2)_2\text{Ni}$, crystallises in lustrous, orange-yellow laminae, m. p. 229°, and the *dibenzoyl* derivative, white prisms, m. p. 112—113°.

Chloromethylglyoxime has m. p. 188—189°. Its *nickel* compound, $\text{C}_6\text{H}_8\text{O}_2\text{N}_2\text{Cl}_2\text{Ni}$, forms lustrous, wine-red plates, and begins to blacken at about 200°.

Nickel acetylhexoyldioxime, $(\text{C}_8\text{H}_{15}\text{O}_2\text{N}_2)_2\text{Ni}$, crystallises in brick-red prisms, m. p. 157—158°. *Nickel acetyl-n-nonoyldioxime*, $(\text{C}_{11}\text{H}_{21}\text{O}_2\text{N}_2)_2\text{Ni}$, crystallises in yellowish-brown plates, m. p. 125°. *Nickel acetyl-palmityldioxime*, $(\text{C}_{18}\text{H}_{35}\text{O}_2\text{N}_2)_2\text{Ni}$, forms yellow plates, m. p. 88—89°. *Nickel acetylstearyldioxime*, $(\text{C}_{20}\text{H}_{39}\text{O}_2\text{N}_2)_2\text{Ni}$, crystallises in orange plates, m. p. 89°. *Nickel phenylmethylglyoxime*, $\text{C}_{18}\text{H}_{18}\text{O}_4\text{N}_2\text{Ni}$, forms scarlet needles, m. p. 239—240. *Nickel methylbenzylglyoxime*, $(\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}_2)_2\text{Ni}$, crystallises in orange laminae, m. p. 180°.

T. H. P.

Chromithiocyanates. I. NIELS BJERRUM (*Z. anorg. Chem.*, 1921, **118**, 131—164).—A detailed study has been made of the formation of complex thiocyanatochromi-compounds from chromium thiocyanate, of their properties, methods of analysis, and of their equilibria in solution. The existence of six different complexes has been established, of which four have been isolated.

Experiments with mixed solutions of chromic nitrate and potassium thiocyanate, in which the formation of chromi-complexes was followed by observing the gradual diminution of the conductivity of the solution, showed that a condition of equilibrium is eventually reached, very slowly in the cold in dilute solution, much more quickly at higher temperatures or at greater concentrations. At the point of equilibrium, the number of (CNS) groups associated with each chromium atom in the complex depends on the ratio of thiocyanate to chromium salt originally present. A mixture of compounds is formed, which can be separated by taking advantage of their

different solubilities in ether. After acidification and extraction with ether, the aqueous solution contains a mixture of monochromipentaquothiocyanate and chromitetraquodithiocyanate salts. The existence of these salts was inferred from analysis of the solution. Their colour in solution is reddish-violet. They are quite stable in acid, but unstable in alkaline solution. The velocity constant in the formation of the mono-complex compound from chromium nitrate and potassium thiocyanate is 0.13 at 50°, the equilibrium constant 328, and the decomposition constant 1.0004 .

Complex chromithiocyanates are also obtained by drying slowly a solution of a hexaquochromithiocyanate. During drying, the colour deepens, the solution becomes syrupy, and eventually indistinct, red crystals of a chromitriaquotrithiocyanate appear. The mixture contains, however, both higher and lower complex thiocyanato-compounds. The trithiocyanato-complex can be extracted with ether, in which the higher tetra-, penta-, and hexa-compounds are not soluble in absence of free acid. It was not found possible to obtain the trithiocyanato-compound perfectly pure, but the analytical figures for the compound approximated to $[\text{Cr}(\text{CNS})_3(\text{H}_2\text{O})_3]$. The aqueous solution is red, but it gives a green solution in ether, with which it forms a compound, probably containing 3 mols. of the solvent. It is quite stable in ether and in acid aqueous solution, but is rapidly decomposed by alkalis, and even by sodium acetate. Determinations of the partition coefficient between water and ether gave results varying from 3.3 to 4.7, and it is supposed from this circumstance that the substance may be a mixture of two stereoisomerides.

The rate of decomposition of potassium chromihexathiocyanate was studied in aqueous, acid, alkaline, and alcoholic solution in the dark and in daylight. In the dark there is not much difference in the rate of decomposition in any of these media; the fact that the hexathiocyanato-compound is not sensitive to alkali confirms the opinion that in the other compounds of the series decomposition by alkali is due to replacement of water in the inner complex by hydroxyl. In daylight, the rate of decomposition is about ten times as fast as in the dark. When an acid solution of the above potassium salt is shaken with ether, three layers are formed, the inner layer being a concentrated solution of chromihexathiocyanato-acid in ether. The acid, however, rapidly decomposes in ether. The following well-characterised, insoluble salts were prepared. *Pyridine* salt, $(\text{C}_5\text{H}_5\text{N})_3\text{Cr}(\text{CNS})_6 \cdot \text{H}_2\text{O}$, reddish-violet, small, flat needles. *Quinoline* salt, $(\text{C}_9\text{H}_7\text{N})_3\text{Cr}(\text{CNS})_6 \cdot \text{H}_2\text{O}$, very small crystals, similar to those of the pyridine salt, with a very small solubility product.

E. H. R.

Chromithiocyanates. II. NIELS BJERRUM (*Z. anorg. Chem.*, 1921, **119**, 39—53; cf. preceding abstract).—After many unsuccessful attempts to isolate a chromiaquopentathiocyanate derivative, this was accomplished by means of the quinoline salt. A solution containing potassium chromihexathiocyanate and

potassium thiocyanate in the mol. ratio 1:3 was heated for two days at 50°, and after acidification first the unchanged chromi-hexathiocyanate and then the chromipentathiocyanate were separately precipitated with quinoline sulphate. Quinoline chromi-aquopentathiocyanate, $[\text{Cr}(\text{CNS})_5\text{H}_2\text{O}](\text{C}_9\text{H}_7\text{N})_3\text{H}_2\text{O}$ forms bluish-violet, small, well developed crystals, readily decomposed by ammonia. An aqueous solution of the sodium salt was obtained by shaking the quinoline salt with ether and aqueous sodium acetate-acetic acid solution. Its colour is reddish-violet; the free acid in ether is greenish-violet, changing to green as it decomposes into the tetrathiocyanato-acid. The rate of decomposition of the chromipentathiocyanato-ion was determined in aqueous acid solutions varying from $p_{\text{H}}=1$ to $p_{\text{H}}=8$. The stability increases with the acid strength; in alkaline solution decomposition is rapid. A solution of chromitetrathiocyanato-acid was prepared from the mixture obtained from the slow drying of a solution of hexaquo-chromic thiocyanate (*loc. cit.*), taking advantage of the fact that the neutral trithiocyanate is extracted by ether from neutral solution, the tetrathiocyanate only after acidification. It is stable in ether, unlike the pentathiocyanate, and forms a green ethereal solution. In water, it forms a reddish-violet solution and is quite stable in presence of acid. No well-defined crystallised salt of the chromitetrathiocyanato-acid was discovered; the quinoline salt is readily soluble and the quinine and strychnine salts form blue, flocculent precipitates of varying composition. E. H. R.

Chromithiocyanates. III. NIELS BJERRUM (*Z. anorg. Chem.*, 1921, **119**, 54—68).—This paper gives an account of the methods used for the analysis of complex mixtures of chromithiocyanato-compounds (preceding abstracts). Chromium was always estimated by titration with thiosulphate after oxidation to chromate with hydrogen peroxide. Titration of a solution of complex chromithiocyanate with silver nitrate by the Volhard method gives the total of ionic thiocyanate plus that present as chromi-tetra-, penta-, and hexa-thiocyanato-ions. The titrated solution is then boiled with sodium hydroxide to decompose chromithiocyanato-complex compounds and after acidification is again titrated by the Volhard process. The second titration gives all the thiocyanate present in the form of chromi-mono-, di-, and tri-thiocyanate compounds plus three thiocyanate groups for each molecule of the chromi-tetra-, penta-, and hexa-thiocyanate compounds. This method is useful only for determining the proportion of ionic and of total complex combined thiocyanate present. The ionic thiocyanate can also be determined colorimetrically with an accuracy of 5—10% by comparing the colour given with ferric nitrate with standard thiocyanate solutions. When a large proportion of complex thiocyanato-chromium compounds is present their colour makes it impossible to use this method. The different complex compounds are estimated as follows. Chromi-hexa- and penta-thiocyanato-compounds are precipitated as quinoline salts, and from an estimation of chromium and thiocyanate in the mixture

the proportion of each can be estimated. The remaining solution is then acidified with sulphuric acid and extracted with ether, after which the ether is again extracted with an aqueous sodium acetate-acetic acid solution. In this way, the trithiocyanate is obtained in the ether and the tetrathiocyanate in the aqueous acetate solution and both can be estimated. The original aqueous solution now contains chromium thiocyanate with chromi-mono- and dithiocyanato-compounds. It is analysed for total chromium and complex combined thiocyanate. An estimation of chromium thiocyanate is made on the original solution by adding potassium sulphate and alcohol, filtering, and analysing the precipitated chrome alum. A small proportion of chromium present as "concealed basic chromium" cannot be estimated in presence of chromi-thiocyanato-compounds. From the data obtained it is possible to estimate approximately the proportions of chromi-mono- and dithiocyanato-compounds present.

E. H. R.

Chromithiocyanates. IV. NIELS BJERRUM (*Z. anorg. Chem.*, 1921, **119**, 179—201; cf. preceding abstracts).—Experiments were made to study the equilibrium between different complex chromi-thiocyanato-compounds at 50°. At the ordinary temperature, the velocity of formation of the complex compounds is extremely slow, but at 50° it proceeds at a speed convenient for measurement. The reaction was followed in solutions of chromic nitrate (0.01*N*) and potassium thiocyanate containing varying proportions of the latter, by means of conductivity measurements, and the solutions were analysed when equilibrium had been reached (cf. Pt. III). Six equilibrium constants are involved, corresponding with the series of six reactions, of which the first is $\text{Cr}(\text{H}_2\text{O})_6^{+++} + \text{CNS}^- = \text{Cr}(\text{H}_2\text{O})_5\text{CNS}^{++} + \text{H}_2\text{O}$, and the last $\text{Cr}(\text{H}_2\text{O})(\text{CNS})_5^{---} + \text{CNS}^- = \text{Cr}(\text{CNS})_6^{---} + \text{H}_2\text{O}$. These constants may be designated $K_{\text{Cr}(\text{CNS})}, K_{\text{Cr}(\text{CNS})_2}, \dots, K_{\text{Cr}(\text{CNS})_6}$, and the values found are 328, 17.5, 4.56, 1.93, 0.81 and 0.41. From these constants can be calculated the affinities of each successive thiocyanate group for the chromium atom. These, calculated from the equation $A = RT \log K$ and expressed in gram-calories are 3710, 1840, 970, 420, -130 and -570. From the equilibrium constants were calculated the proportions of each of the complex chromi-thiocyanato-compounds which will be present in solution in chemical equilibrium for concentrations of ionic thiocyanate from 10^{-3} to 10 molar, and these results are embodied in a diagram by means of which the concentration of each complex compound can be found when the thiocyanate-ion concentration is known. A curve is given showing the relation between the concentration of ionic thiocyanate and the number of combined thiocyanate groups per atom of chromium. At 100°, equilibrium is reached in about half an hour, but apparently a rather smaller proportion of complex compounds is present at equilibrium. On the other hand, a solution which had stood for several years at room temperature showed a greater proportion of higher complex compounds than a solution of the same total concentration in equilibrium at 50°.

E. H. R.

Preparation of Organic Compounds of Boron with the Aid of Boron Fluoride. I. Boron Alkyls and Alkylboric Acids. ERICH KRAUSE and RUDOLF NITSCHKE (*Ber.*, 1921, 54, [B], 2784—2791).—Boron trialkyls are prepared readily by passing gaseous boron trifluoride (prepared from potassium borofluoride, boric anhydride, and concentrated sulphuric acid and purified by condensation by liquid air and subsequent fractionation of the liquefied gas) into an ethereal solution of the requisite Grignard's reagents. They are isolated by distillation of the crude product of the reaction (under diminished pressure, if necessary) in an atmosphere of nitrogen. They are colourless, mobile liquids with a not unpleasant odour. They are readily oxidised on exposure to air, frequently becoming spontaneously ignited. They can be preserved indefinitely, even if exposed to light, in an atmosphere of nitrogen in sealed tubes. In spite of their relatively high boiling points, they are readily volatile at the atmospheric temperature. They are very slowly decomposed by water. The alkylboric acids, $\text{Alk}\cdot\text{B}(\text{OH})_2$, are most conveniently prepared by preserving the boron trialkyls in a loosely-stoppered flask originally filled with nitrogen; in consequence of the inward diffusion of air, they then become oxidised gradually to the boronalkyl oxides, $\text{Alk}\cdot\text{B}_2\text{O}$, which are converted by crystallisation from a small quantity of hot water into the alkylboric acids. The latter are crystalline compounds which are very soluble in the usual media. They reduce alcoholic silver nitrate solution when warm, but not in the cold. Their volatility is remarkable.

Boron triisocamyl, $\text{B}(\text{C}_5\text{H}_{11})_3$, has b. p. $119^\circ/14$ mm., d_4^{25} (vac.) 0.7600, n_D^{25} (vac.) 0.7607, $n_{\text{H}_2}^{25}$ 1.42983, n_D^{25} 1.43207, $n_{\text{H}_2}^{25}$ 1.43782, $n_{\text{H}_2}^{25}$ 1.44254. *Boron triisobutyl* has b. p. $86^\circ/20$ mm., $188^\circ/760$ mm., d_4^{25} (vac.) 0.7380, whence d_4^{25} (vac.) 0.7400, $n_{\text{H}_2}^{25}$ 1.41652, n_D^{25} 1.41882, $n_{\text{H}_2}^{25}$ 1.42445, $n_{\text{H}_2}^{25}$ 1.42882. *Boron tri-n-propyl*, b. p. $60^\circ/20$ mm., $156^\circ/760$ mm., has d_4^{25} (vac.) 0.7024, whence d_4^{25} (vac.) 0.7225, $n_{\text{H}_2}^{25}$ 1.41129, $n_{\text{H}_2}^{25}$ 1.41352, $n_{\text{H}_2}^{25}$ 1.41895, $n_{\text{H}_2}^{25}$ 1.42354.

isoAmylboric acid, $\text{C}_5\text{H}_{11}\cdot\text{B}(\text{OH})_2$, colourless, rectangular plates, m. p. 169° , *isobutylboric acid*, long, colourless, pointed plates, m. p. 112° , and *n-propylboric acid*, thick, rectangular plates, m. p. 107° , are described.

H. W.

Constitution of Grignard's Compounds. JULIUS VON BRAUN (*Ber.*, 1921, 54, [B], 2687).—The idea that the primary product of the interaction of a Grignard reagent with a carbonyl compound is a molecular additive product (Meisenheimer and Caspar, A., 1921, i, 654) has been advanced previously by the author (A., 1918, i, 107; 1920, i, 30). He, however, has regarded the addition as occurring at the oxygen atom, whereas Meisenheimer and Caspar consider it to take place at the magnesium atom.

H. W.

Lignite Producer Tar. S. RUEHMANN (*Ber.*, 1921, 54, [B], 2565—2568).—A preliminary account. The crude tar is dehydrated, freed from mechanical impurities, distilled under diminished

pressure (about 20 mm.), and finally treated with steam at 100°. The investigation of the neutral oils and phenols is confined for the present to the steam distillate, whereas the total vacuum distillate is used for the examination of the acids. The neutral oils are collected in a number of fractions between 83 and 166°/12 mm. The separate portions are characterised by a pleasant odour and deep blue fluorescence which gives place after a time to a dark brown coloration. They all contain sulphur (3.4—1.8%) which is removed only to a small extent by distillation over sodium, but can be considerably eliminated by treatment with sodium in boiling alcoholic solution; oxygen is also present. Further purification is conveniently effected by agitating them with methyl alcohol, which dissolves the greater proportion of the sulphur and the whole of the oxygen compounds and gives a residue containing essentially paraffins and naphthenes. The latter are readily destroyed by treatment with fuming nitric acid. A neutral fraction, b. p. 140—145°/12 mm. when treated in this manner, yielded a product, b. p. 144—147°/12 mm., which appears to be hexadecane or the next higher homologue.

The portion of the tar soluble in sodium carbonate solution appears to contain acids of the series $C_nH_{2n-2}O_2$ and $C_nH_{2n-4}O_2$, the investigation of which is not complete.

The sodium hydroxide extract of the tar consists essentially of phenols which distil at 88—178°/12 mm., with considerable formation of pitch. They can be most readily separated from one another by conversion into the arylurethanes, $NH_2 \cdot CO \cdot O \cdot Ar$, and crystallisation of the latter from a mixture of benzene and light petroleum. Regeneration is effected by heating the esters when they are decomposed into the phenols and cyanic acid. The presence of cresol and its three next higher homologues has been established. Phenol appears to be absent.

H. W.

Sulphuryl Chloride. I. Influence of Catalysts: a Convenient Method of Chlorinating Benzene. OSWALD SILBERRAD (T., 1921, 119, 2029—2036).

The *o*- and *p*-Nitrobenzyl Bromides. CHARLES MOUREU and RALPH L. BROWN (*Bull. Soc. chim.*, 1921, [iv], 29, 1006—1008).—*o*-Nitrobenzyl bromide may readily be obtained by the action of either hydrogen bromide or phosphorus pentabromide on *o*-nitrobenzyl alcohol in chloroform solution (cf. Norris, Watt, and Thomas, A., 1916, i, 461). *p*-Nitrobenzyl bromide is obtained with a 30% yield by the direct nitration of benzyl bromide (cf. Lyons and Reid, A., 1917, i, 559).

W. G.

The Action of Cupric Chloride on Organometallic Derivatives of Magnesium. EUSTACE EBENEZER TURNER (*J. Roy. Soc. New South Wales*, 1920, 54, 37—39).—The method of preparing diphenyl by the interaction of magnesium phenyl bromide in ethereal solution and anhydrous cupric chloride (cf. T., 1919, 115, 559) was found to be successful for the preparation of 1:1'-ditolyl, but could not be used for coupling two dissimilar groups.

Cupric chloride did not react with the magnesium derivatives of halogenated fatty acids to give succinic acids, but ethyl α -bromobutyrate reacted in ethereal solution with magnesium and cupric chloride, giving ethyl *s*-dichylsuccinate. W. G.

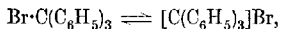
The Behaviour of Azo-compounds and their Salts with Aromatic Hydrocarbons and Aluminium Chloride. RUDOLPH PUMMERER and JOSEPH BINAPFL (*Ber.*, 1921, 54, [B], 2768—2784).—An attempt has been made to extend Scholl's condensations with aluminium chloride in the anthracene and naphthalene series to the benzene series by carrying out the reactions in presence of a substance, such as azobenzene, capable of undergoing hydrogenation. It is uncertain whether diphenyl is formed, for the greater part of the benzene is converted into viscous, high molecular condensation products, thus benzene and aluminium chloride begin to react at 40°, but no gaseous hydrogen can be detected. Bisdiphenylene-ethylene, however, when dissolved in dry xylene, b. p. 135—138°, and treated with five equivalents of aluminium chloride for twelve hours at 35—40°, is converted into bisdiphenylene-ethane (67% yield), long, glistening needles from benzene and alcohol, m. p. 238.5—239°. The hydrogenating action of dry benzene, free from thiophen, and aluminium chloride on azobenzene for three-quarters of an hour at 60° results in the formation of hydrazobenzene in 18% yield. In presence of hydrogen chloride, phenylation occurs with the formation of aminodiphenyl, m. p. 53°, in a yield of 70—80%, together with 10% of benzidine, some aniline, and 7—10% of an oxidisable substance which is possibly a semidine base. The course of the reaction in the formation of the aminodiphenyl is probably as follows: $\text{NPh:NPh} + \text{C}_6\text{H}_6 \rightarrow \text{NHPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_5\text{Ph}$; $\text{NHPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_5\text{Ph} \rightarrow \text{NPh:N}\cdot\text{C}_6\text{H}_5\text{Ph}$; $\text{NPh:N}\cdot\text{C}_6\text{H}_5\text{Ph} + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5\text{Ph}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_5\text{Ph}$; $\text{C}_6\text{H}_5\text{Ph}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_5\text{Ph} + 2\text{H} \rightarrow 2\text{C}_6\text{H}_5\text{Ph}\cdot\text{NH}_2$; which is equivalent to: $\text{NPh:NPh} + 2\text{C}_6\text{H}_6 = 2\text{C}_6\text{H}_5\text{Ph}\cdot\text{NH}_2$. This reaction is not limited to the use of azobenzene and benzene, for a similar reaction proceeds even more readily when the latter is replaced by toluene or xylene. F. M. R.

The Alleged Hexavalency of Carbon in Carbonium and Dyestuff Salts. A. HANTZSCH (*Ber.*, 1921, 54, [B], 2569—2572).—Kehrmann's theory of the hexavalency of carbon in carbonium salts (*A.*, 1918, i, 311) is refuted, and is shown to be entirely lacking in experimental support. The extension of Kehrmann's theory to the yellow salts obtained from fuchsonimonium chloride and to the salts of aminoazo-colouring matters (*A.*, 1917, i, 593) is equally unsound. F. M. R.

The Constitution of Carbonium Salts. A. HANTZSCH (*Ber.*, 1921, 54, [B], 2573—2613).—Determination of the absorption spectra, conductivity measurements, and chemical investigation show the existence of only two sharply-defined groups of triphenylmethane derivatives, which are interconvertible, and which give rise to equilibrium mixtures. In addition to the normally-con-

stituted, colourless, non-conducting triphenylmethane compounds there exist only the well-characterised, anomalous, yellow conducting triphenylcarbonium salts, which may be recognised by their absorption spectra. The latter compounds are not to be regarded as compounds which possess "ionisable" carbon valencies, or individual unsaturated carbon atoms, or quinonoid or quinolide rings, as has been the case hitherto, but are to be regarded as carbonium salts similarly constituted to the azonium, phosphonium, oxonium, and thionium salts. As is usually the case with -onium haloids, two series of isomeric halogen derivatives exist in the case of the carbonium compounds, viz., pseudo-salts with a direct non-ionising linking of the halogen atom, such as $X \cdot C(C_6H_5)_3$, and true salts with an indirect ionising linking of the halogen atom, such as $[C(C_6H_5)_3]X$.

Under suitable conditions the compounds are partly isomerised when dissolved in inert solvents with the formation of an equilibrium mixture, thus :



the tendency being towards the formation of the pseudo-salt. The more readily and completely the halogen atom forms complex anions with chemically active substances, the greater the tendency of the equilibrium towards the formation of the carbonium salt containing the complex kation $[C(C_6H_5)_3]$.

Even the carbonium perchlorate in an inert solvent such as chloroform is converted into the pseudo-salt with the formation of the equilibrium mixture :



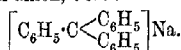
Ether, in suitable concentrations, converts all the equilibrium mixtures into colourless solutions of the pseudo-salts, but, in the case of the pseudo-perchlorate, when the ether is removed, isomerisation occurs and the true salt is formed. The chemical behaviour of carbonium salts also can only be explained by the complex formula $[C(C_6H_5)_3]X$. As is the case with all groups attached directly to the central atom of a complex kation, the benzene nucleus in carbonium salts cannot be detected by its usual reactions, such as bromination, sulphonation, or nitration. The carbonium salts are structurally related to the diazonium salts, as is shown by the common possession of several characteristic reactions; for example, alcohol converts triphenylcarbonium salts into triphenylmethane in a similar manner to the conversion of benzenediazonium salts into benzene.

The yellow salts of rosaniline dyes formed in strongly acid solution are also carbonium salts, thus pararosaniline forms tri-anilino-sulphato-carbonium sulphate, $[C(C_6H_4 \cdot NH_2)_3]SO_4H$.

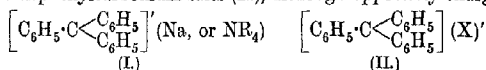
F. M. R.

The Coloured Alkali Salts of Triphenylmethane, and Triphenylmethyl as an Amphoteric Ion. A. HANTZSCH *Ber.*, 1921, **54**, [B], 2613—2620).—The proof that the coloured salts of triphenylcarbinol are true -onium salts (cf. preceding abstract) in which the triphenylmethyl residue functions as a

kation leads to the conclusion that the coloured alkali salts, such as triphenylmethyl-sodium, are neither true triphenylmethane derivatives with an ionisable carbon valency nor quinonoid compounds, but are also complex salts in which the triphenylmethyl residues function as an anion, thus :



In the same manner that the neutral triphenylmethyl residue in the colourless, non-conducting triphenylmethyl compounds, $\text{R} \cdot \text{C}(\text{C}_6\text{H}_5)_3$, acts as kation in combination with strongly negative acidic residues or anions, it acts as anion when combined with strongly positive metals or kations. Consequently, alkali and tetra-alkylammonium salts (I) are chemically similarly constituted to the triphenylcarbonium salts (II), although oppositely charged :



Just as the triphenylcarbonium salts are derived from the similarly coloured true base, $[\text{C}(\text{C}_6\text{H}_5)_3]\text{OH}$, which is spontaneously isomerised to the colourless pseudo-base, $\text{HO} \cdot \text{C}(\text{C}_6\text{H}_5)_3$, so the coloured alkali salts are derived from the true colour acid, $[\text{C}(\text{C}_6\text{H}_5)_3]\text{H}$, which is spontaneously isomerised to the colourless pseudo-acid, $\text{H} \cdot \text{C}(\text{C}_6\text{H}_5)_3$.

There is, therefore, an analogy with the *aci*-trinitromethane salts, and consequently the coloured metallic salts of triphenylmethane are *aci*-triphenylmethane salts. Colourless pseudo-metallic salts, such as $\text{MgCl} \cdot \text{C}(\text{C}_6\text{H}_5)_3$, or $\text{Zn}(\text{CH}_3 \cdot \text{C}_6\text{H}_5)_3$, also exist and correspond with the colourless pseudo-haloid salts, $\text{X} \cdot \text{C}(\text{C}_6\text{H}_5)_3$.

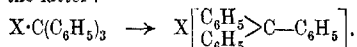
F. M. R.

The So-called Halochromism of Triphenylmethane Derivatives. A. HANTZSCH (*Ber.*, 1921, **54**, [B], 2620—2627).—A. von Baeyer's conception of halochromism rests on a purely empirical basis and merely expresses the fact that certain colourless substances are converted into coloured salts by means of colourless acids or bases, without explaining the phenomenon. In the author's opinion, halochromism is produced by a discontinuous chemical reaction resulting in an alteration in structure, such as the alternate transition between an ionogenic and non-ionogenic linking, that is, isomerism between electrolytes and non-electrolytes. As it has been shown by optical measurements that normal salt formation from true acids, which occurs without any structural alteration, is an optically indifferent process, it follows that halochromism does not occur without structural alteration. Kauffmann's recent work on the derivation of valency laws (*A.*, 1920, i, 50) is discussed and his deductions are refuted.

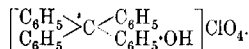
F. M. R.

The Co-ordination Number of Carbon. A. HANTZSCH (*Ber.*, 1921, **54**, [B], 2627—2633).—As the haloid pseudo-salts of triphenylmethyl are isomerised under suitable conditions to the true triphenylcarbonium haloids, it follows that the normally

quadrivalent carbon atom in the former possesses the co-ordination number 3 in the latter :



Carbon retains this co-ordination number also in all other electrolytes in which it is the central atom of kations or anions, for example, in the yellow carbonium salts which contain more than two equivalents of acid to one of base, such as $[C(C_6H_5)_3 \cdot NH_3 \cdot SO_4H_2]SO_4H_2$, and in the red anions of the alkali salts, such as $[CH_3 \cdot C_6H_5]Na$, $[CH(C_6H_5)_2]Na$, $[C(C_6H_5)_3]Na$, etc. Under suitable conditions, the co-ordination number of carbon in the kation of the carbonium salts can be raised from 3 to 4, particularly in media which dissolve these salts without decomposition, thus :



F. M. R.

Catalytic Oxidation of Naphthalene. C. R. DOWNS (U.S. Pat. 1374722).—Naphthalene vapour is partly oxidised to form phthalic anhydride by subjecting it to the action of an oxidising gas such as air at a temperature of about 450° in the presence of aluminium oxide as a catalyst.

CHEMICAL ABSTRACTS.

Catalytic Oxidation of Fluorene. J. M. WEISS and C. R. DOWNS (U.S. Pat. 1374695).—Fluorenone is produced by oxidising fluorene vapour with air at a temperature of 300–700° in the presence of a catalytic metal oxide.

CHEMICAL ABSTRACTS.

Determination of the Melting- and Boiling-points of Anthracene, Phenanthrene, and Carbazole. W. KIRBY (*J. Soc. Chem. Ind.*, 1921, 40, 274r).—Determinations of the melting- and boiling-points of anthracene, phenanthrene, and carbazole, using specially purified materials, gave the following results: anthracene, m. p. 218°, b. p. 340°; phenanthrene, m. p. 101°, b. p. 332°; carbazole, m. p. 247°, b. p. 351.5°. Earlier recorded values were generally lower in the case of the melting-points and higher in the case of the boiling-points.

G. W. R.

o-Quinones and 1:2-Diketones. IV. Synthesis of Acenaphthene. A. SCHÖNBERG (*Ber.*, 1921, 54, [B], 2838–2839).—A preliminary note. A suitable synthesis of acenaphthene and its derivatives has not been described previously. It is now shown that acenaphthenedisemicarbazone gives a 50% yield of acenaphthene when heated at 200° with a solution of sodium in alcohol (cf. Wolff, A., 1912, i, 988). The application of the synthesis to derivatives of acenaphthene is being investigated.

H. W.

New Derivatives of Diphenylamine. A. V. BLOM (*Hdv. Chim. Acta*, 1921, 4, 1036–1039).—The following new derivatives of diphenylamine are described: 4'-chloro-2:4-dinitrodiphenylamine, orange-red needles, m. p. 166°, which on reduction with

sodium sulphide and alcohol yields 4'-chloro-4-nitro-2-amino-diphenylamine, brownish-violet needles, m. p. 177°; 2:4-dinitro-4'-ethoxydiphenylamine, glistening, red plates, m. p. 119—120°, which on reduction yields 4-nitro-2-amino-4'-ethoxydiphenylamine, brown plates, m. p. 153°; 2:4-dinitro-4'-methoxydiphenylamine, dark red, glistening needles, m. p. 140°; 4:4'-dichloro-2-nitro-diphenylamine, reddish-brown, glistening needles, m. p. 149—150°.

In an attempt to prepare carbazole derivatives, the above nitro-aminodiphenylamine derivatives were converted into the azimines, but nitrogen could not be removed from the latter; 4'-chloro-4-nitrophenylaziminobenzene, forms brown needles, m. p. 212—213°, and on reduction and acetylation yields 4'-chloro-4-acetylaminophenylaziminobenzene, silvery needles, m. p. above 300°; 4-nitro-4'-ethoxyphenylaziminobenzene, crystallised in pale brown needles, m. p. 145—146°.

F. M. R.

The History of the Blue Oxidation Product from Diphenylamine. F. KEHRMANN and ST. MICEWICZ (*Helv. Chim. Acta*, 1921, 4, 949).—Blom's view (A., 1921, ii, 664) that the cause of the colour reaction between diphenylamine, nitric acid, and sulphuric acid is still undecided is corrected (cf. Wieland and Müller, A., 1913, i, 1386; Kehrman and Micewicz, A., 1912, i, 1020). The authors, in their former publication (*loc. cit.*), attributed the discovery of this reaction to Merz and Weith (*Ber.*, 1872, 5, 283), whereas it was actually due to A. W. Hofmann (*Annalen*, 1864, 132, 165).

F. M. R.

Ketens. XXXVII. Ketenimine Derivatives. H. STAUDINGER and E. HAUSER (*Helv. Chim. Acta*, 1921, 4, 887—896).—It has been shown previously (Staudinger and Meyer, A., 1920, i, 228) that a ketenimine derivative is prepared by the action of triphenylphosphinephenylimine with diphenylketen thus: $\text{PPh}_3\text{:NPh} + \text{CPh}_2\text{:C:O} \rightarrow \text{PPh}_3\text{:O} + \text{CPh}_2\text{:C:NPh}$. The same substance can also be obtained from triphenylphosphinediphenylmethylene and phenylcarbimide: $\text{PPh}_3\text{:CPh}_2 + \text{NPh:CO} \rightarrow \text{PPh}_3\text{:O} + \text{CPh}_2\text{:C:NPh}$. The former reaction occurs with greater readiness and smoothness, however, and has now been subjected to an extended examination. Differently substituted ketens, which in other reactions exhibit such unusual diversity, react with about equal ease with phosphineimine derivatives. On the other hand, diphenylketen reacts much more readily with alkylated than with arylated phosphineimines (cf. Staudinger and Hauser, this vol., i, 68). When the act is considered that the replacement of the carbonyl by the CN·R group usually causes enhanced activity, it is remarkable to find that the ketenimine compounds are highly stable. They do not suffer autoxidation and do not unite with unsaturated compounds. They are generally stable towards water and alcohol, but are hydrolysed by acids to the corresponding acid amides. They react fairly readily with aniline and phenylhydrazine, but much less vigorously than do the ketens. On the other hand, the ease with which the simple ketenimines undergo polymerisation is surprising in such stable substances.

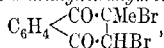
Diphenylketenphenylimine, $\text{CPh}_2\text{:C:NPh}$ (*loc. cit.*), is converted by aniline into diphenylacetodiphenylamidine, m. p. 114° , and by phenylhydrazine into the compound, $\text{CHPh}_2\text{:C(N:NHPh):NHPH}$, m. p. 117° . It undergoes autoxidation at 150° , partly in accordance with the scheme: $\text{CPh}_2\text{:C:NPh} + \text{O}_2 \rightarrow \text{COPh}_2 + \text{O:C:NPh}$. Triphenylphosphinemethylimine and diphenylketen give triphenylphosphine oxide and *diphenylketenmethylimine*, $\text{CPh}_2\text{:C:NMe}$, a yellow liquid, b. p. $120^\circ/0.2$ mm., which could not be obtained quite pure. It is a very stable substance which shows little tendency towards polymerisation; it is converted by concentrated hydrochloric acid into *diphenylacetomethylamide*, colourless crystals, m. p. 164.5° . In contrast with diphenylketenaphthenylimine, the methyl compound unites with methyl iodide, but the methiodide has not been examined further. *Dimethylketenphenylimine*, $\text{CMe}_2\text{:C:NPh}$, is a pale yellow liquid, b. p. $98-100^\circ/12$ mm.; it is transformed by concentrated hydrochloric acid into *isobutyramide*, m. p. 104° . *Ketenphenylimine*, $\text{CH}_2\text{:C:NPh}$, a colourless, mobile liquid, b. p. $35^\circ/0.1$ mm., which solidifies to a colourless, crystalline mass at about -40° , is prepared from triphenylphosphinephenylimine and keten in light petroleum solution at -20° . It readily becomes polymerised to a black, amorphous solid when preserved, but is otherwise surprisingly stable; it does not appear to react with water, alcohol, benzaldehyde, dimethylaminobenzaldehyde, benzyldencaniline, thiobenzophenone, azidocarbonyl ester, or quinoline and carbon disulphide. Concentrated hydrochloric acid transforms it immediately into acetanilide. *Ketenethylimine*, $\text{CH}_2\text{:CH:NEt}$, could not be isolated with certainty by reason of the readiness with which it polymerises even at -20° . *Ethyl phenylimineketendicarboxylate*, $\text{XPh:C:C(CO}_2\text{Et)}_2$, forms colourless crystals, m. p. $80-83^\circ$; it is much more sensitive to moisture than the products described above. H. W.

The 2-Methylnaphthalene Series. K. FRIES and W. LOHMANN (*Ber.*, 1921, **54**, [B], 2912-2924).—Previous experiments have shown that 1-methyl- β -naphthol is very readily converted into derivatives of 1:2-dihydronaphthalene under the influence of mild oxidising agents (A., 1906, i, 190). Under similar conditions, 4-chloro-2-methyl- α -naphthol is transformed into 2-methyl-1:4-naphthaquinone.

2-Methyl- α -naphthylamine is prepared conveniently by reducing 1-nitro-2-methylnaphthalene with tin and hydrochloric acid and is converted by chlorine in the presence of glacial acetic acid and fuming hydrochloric acids into 1-*keto*-2-methyl-2:3:4:4-tetrachlorotetrahydronaphthalene, $\text{C}_6\text{H}_4\begin{matrix} \text{C} & \text{C} \\ \diagup & \diagdown \\ \text{O} & \text{Me} \\ \diagdown & \diagup \\ \text{C} & \text{C} \\ \diagup & \diagdown \\ \text{Cl}_2 & \text{CHCl} \end{matrix}$, colourless, prismatic crystals, m. p. 118° . The latter is attacked but slowly by reducing agents, and does not liberate iodine from potassium iodide. It is converted by stannous chloride in glacial acetic acid solution into 4-chloro-2-methyl- α -naphthol, colourless needles, m. p. 104.5° (*acetate*, needles, m. p. 87°), which is oxidised by an excess of aqueous ferric chloride (less readily by hydrogen peroxide, nitrous or nitric acids)

to 2-methyl-1:4-naphthaquinone, long, yellow needles, m. p. 104°; the quinone is prepared more easily by the oxidation of a solution of 2-methyl- α -naphthylamine sulphate in boiling glacial acetic acid with hydrogen peroxide. It is reduced by stannous chloride in the presence of glacial acetic acid to 1:4-dihydroxy-2-methylnaphthalene, colourless needles, m. p. (indefinite) 160°, after incipient darkening at about 120° (diacetate, prisms, m. p. 113°). Chlorine converts the quinone or quinol into 2:3-dichloro-1:4-diketo-2-methyltetrahydronaphthalene, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{MeCl} \\ \text{CO} \cdot \text{CHCl} \end{smallmatrix}$, small, pale yellow

crystals, m. p. 45.5°, which is transformed, slowly by stannous chloride and boiling glacial acetic acid but more rapidly by hot concentrated sulphuric acid, into 3-chloro-2-methyl-1:4-naphthaquinone, dark yellow needles, m. p. 153°. It is remarkably stable towards aniline. Reduction with stannous chloride transforms it into 3-chloro-1:4-dihydroxy-2-methylnaphthalene, long needles, m. p. (indefinite) 160°, after darkening at 130° (diacetate, slender, colourless needles, m. p. 194°). The action of bromine on 2-methyl-1:4-naphthaquinone gives a mixture of 3-bromo-2-methyl-1:4-naphthaquinone, yellowish-brown needles, m. p. 151°, and 2:3-dibromo-1:4-diketo-2-methyltetrahydronaphthalene,



coarse, pale yellow prisms, m. p. 107°. 3-Bromo-1:4-dihydroxy-2-methylnaphthalene crystallises in colourless prisms or needles, which darken above 95°, but do not appear to melt (diacetate, colourless needles, m. p. 209°).

If hydrogen peroxide is added cautiously to a solution of 2-methyl- α -naphthylamine sulphate in boiling glacial acetic acid, the separation of 4:4'-diamino-3:3'-dimethyldinaphthyl sulphate is observed. The free base forms colourless, prismatic crystals, m. p. 213° (diacetyl derivative, m. p. above 300°). The presence of two free amino-groups in the molecule is proved by its conversion into the di-*p*-nitrobenzylidene compound, $C_{35}H_{26}O_4N_4$, small red crystals.

H. W.

Chromo-isomeric Silver Salts of Pentabromophenol, and a Theory of Chromo-isomerism of Solid Compounds. HOWARD J. LUCAS and ARCHIE R. KEMP (*J. Amer. Chem. Soc.*, 1921, **43**, 1654—1665).—The silver salt of pentabromophenol exists in two forms, one pink and the other colourless, and in both forms silver is linked to oxygen. The moist pink salt is converted into the more stable, colourless form on heating or in the presence of a small amount of alcohol or of ammonia. If treated with stronger aqueous ammonia, it is converted into a white ammoniate, $C_6Br_5O \cdot NH_3 \cdot C_6Br_5OAg \cdot 2NH_3 \cdot H_2O$, which changes into a yellow ammoniate, $C_6Br_5OAg \cdot 2NH_3$, when warmed with stronger ammonia solutions. The pink salt is more reactive than the white salt. Thus with ethyl iodide it more readily gives the ethyl ether, and it more rapidly absorbs ammonia from an atmosphere containing it. To explain these facts, a new theory of chromo-isomerism is

proposed, on the basis of which the wave-length of the light absorbed by a substance will change as the electrostatic environment of the absorbing atoms or ions changes, and will be longest when the electrostatic fields are the strongest. This theory offers a satisfactory explanation of the yellow colour of aqueous solutions of the colourless sodium pentabromophenoxide, of the colour of the two forms of the silver salt, and of the yellow colour of the ammoniate of the latter. Absorption of light in these cases is attributed to the isorropesis of the benzene ring, which is undoubtedly a factor in colour production in other benzene derivatives.

The theory offers a satisfactory explanation of the different colours of polymorphic forms of inorganic compounds such as mercuric iodide, thallic iodide, etc. The more symmetrical form is the darker coloured because the electrostatic fields about the atoms are stronger in the more symmetrical forms. W. G.

Production of Picric Acid from the Sulphonic Acids of Phenol. RUTH KING (T., 1921, 119, 2105—2119).

Preparation of *p*-Methylaminophenol. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Swiss Pat., 88561; from *Chem. Zentr.*, 1921, 7, 803—804).—*p*-Arylsulphonamidophenyl esters of the formula $\text{cyl}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{SO}_2\cdot\text{Aryl}$ are methylated on the *N*-hydrogen atom and the monomethyl derivatives thus obtained are hydrolysed to form *p*-methylaminophenol by the usual methods. By treatment of 4-toluenesulphonamidophenyl toluenesulphonate, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$, with sodium hydroxide solutions, the sodium salt is obtained as leaf-like, white crystals. This is heated with methyl alcohol and methyl chloride under pressure for a few hours at 100—120°, whereby 4-toluenesulphonmethylamido-phenyl toluenesulphonate is obtained; it forms needles, m. p. 162°. This is heated with 70% sulphuric acid, and by cautious addition of water to the brown product a clear solution is obtained, which is treated with dilute sodium carbonate solution, *p*-methylaminophenol is extracted from the weak alkaline solution with ether.

G. W. R.

Metallic Derivatives of Nitrophenolic Compounds. II. Some Nitrotyloxydides of Metals of Group II. DOROTHY GODDARD and ARCHIBALD EDWIN GODDARD (T., 1921, 119, 2044—2048).

Thymol from Nitrocymene. R. M. COLE (U.S. Pat., 1378939).—Thymol is prepared by electrolytic reduction of nitrocymene and diazotisation and reduction of the resulting 2-amino-5-hydroxy-1-methyl-4-isopropylbenzene. CHEMICAL ABSTRACTS.

Preparation of Thymol, Menthone, and Menthol from Eucalyptus Oils. HENRY G. SMITH and A. R. PENFOLD (*J. Roy. Soc. New South Wales*, 1920, 54, 40—47; cf. T., 1921, 119, 779).—Piperitone, a natural constituent of certain eucalyptus oils (*loc. cit.*), when oxidised with ferric chloride and acetic acid, gives a 25% yield of thymol. When reduced by hydrogen in the presence

of nickel at 175—180°, piperitone gives an almost quantitative yield of menthone, which on further treatment with sodium in aqueous ether gives menthol.

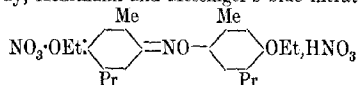
W. G.

Oxonium Salts from Phenol Ethers and Phenols. I. Nitrosophenol Dyes. IV. F. KEHRMANN, H. DECKER, and B. SOLONINA (*Ber.*, 1921, **54**, [B], 2427—2435).—With reference to Decker and Solonina's quinonoid oxonium formula for Kehrman and Messinger's colour salt from thymol ethyl ether (*A.*, 1902, i, 767), Meyer and Billroth (*A.*, 1920, i, 37) state that the compound was not purified by crystallisation, and that the constitution of the diphenylamine derivative obtained by reduction was not definitely proved. These assertions are controverted by the authors, who apply the oxonium theory to explain the constitution of other similar compounds.

T. H. P.

Oxonium Salts from Phenol Ethers and Phenols. II. Decomposition of Oxonium Salts from Thymol Ethyl Ether and from Anisole by Water or Substances of Alkaline Reaction. F. KEHRMANN, H. DECKER, and CH. SCHMAJEWSKI (*Ber.*, 1921, **54**, [B], 2435—2440).—The authors have investigated further the red compounds obtained from oxonium salts by the action of basic compounds or water (Decker and Solonina, *A.*, 1902, i, 767).

In this way, Kehrman and Messinger's blue nitrate,



(cf. Meyer and Billroth, *A.*, 1920, i, 37), yields a mixture, from which the following two compounds have been isolated: (1) Thymindophenol ethyl ether (Decker and Solonina, *loc. cit.*), and (2) a small proportion of a compound, crystallising in pale orange-yellow needles, m. p. 125—126°, and of unknown constitution; the expected diethyl ether of dithymylnitric oxide was not detected.

When dianisylnitric oxide is prepared by the action of pyridine on the perchlorate of the blue compound formed by nitration of anisole (Meyer and Billroth, *loc. cit.*), it is accompanied by *indophenol oxide monomethyl ether*, $\text{O}:\begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_3 \\ \diagdown \quad \diagup \end{array}=\text{NO}-\begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_3 \\ \diagdown \quad \diagup \end{array}\text{OMe}$, which

crystallises in lustrous, pale orange-yellow needles, m. p. 125—126°, forms a violet solution in concentrated sulphuric acid, and is reduced by stannous chloride to *p*-hydroxy-*p'*-methoxydiphenylamine. By ferric chloride, the latter is oxidised to *indophenol monomethyl ether*, which crystallises in lustrous, yellowish-red, unstable crystals, and may be prepared from the potassium derivative of indophenol, by way of the corresponding silver compound.

T. H. P.

Studies in the Dihydronaphthalene Series. II. The *ar*-Dihydro-*a*-naphthols and their Derivatives. FREDERICK MAURICE ROWE and ESTHER LEVIN (*T.*, 1921, **119**, 2021—2029).

Nitro-Derivatives of Quinol. F. KEHRMANN, M. SANDOZ, and R. MONNIER (*Helv. Chim. Acta*, 1921, 4, 941—948).—The observation that quinol monobenzoate is nitrated when dissolved in amyl nitrite led to this investigation of the quinol benzoates. The nitration of quinol monobenzoate, m. p. 163—164°, in acetic acid solution with one molecular proportion of nitric acid yields 2-nitroquinol 4-monobenzoate, golden-yellow needles, m. p. 95—96°, identical with that obtained by the action of amyl nitrite. Hydrolysis converts it into *o*-nitroquinol, m. p. 133—134° (Elbs, A., 1893, 640), and benzoylation yields *o*-nitroquinol dibenzoate, white, silky needles, m. p. 139—140°. Further nitration yields 2:6-dinitroquinol 4-benzoate, citron-yellow needles, m. p. 150—151°, which on hydrolysis is converted into 2:6-dinitroquinol, long, yellow needles containing water of crystallisation, m. p. 134—135° (Nietzki, A., 1883, 465); 2:6-dinitroquinol 4-nitrobenzoate, straw-yellow needles, m. p. 161—162°; *o*-nitroquinol dinitrobenzoate, small, white crystals, m. p. 214—215°.

The nitration of quinol dibenzoate, m. p. 180—181°, yields 2:6-dinitroquinol dinitrobenzoate, yellow needles, m. p. 158—159°. It is interesting to note that two nitro-groups enter the quinol nucleus in this case, whereas a second nitro-group cannot be introduced into the quinol nucleus by the nitration of 2-nitroquinol dibenzoate. The nitration of quinol dibenzoate never results in the formation of a mononitro-derivative, which is in agreement with Nietzki's observations (*loc. cit.*) with quinol diacetate. F. M. R.

Nuclear Condensations of Ethers of Phenylmercaptan. I. A. BISTRZYCKI and FRANZ KUBA (*Helv. Chim. Acta*, 1921, 4, 969—981).—*p*-Methylthioltriphenylacetic acid, $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$, colourless needles or microscopic prisms, m. p. 208—210° after softening at 204°, is prepared in almost quantitative yield by the gradual addition of anhydrous stannic chloride to a gently boiling solution of benzoic acid and anisyl mercaptan in benzene. The silver salt and methyl ester, colourless prisms, m. p. 141—142.5°, are described. Attempts to demethylate the acid by hydriodic acid or aluminium chloride alone or in the presence of benzene or carbon disulphide did not lead to the desired result. The acid is converted by sulphuric acid (95%) at the atmospheric temperature into *p*-methylthioltriphenylcarbinol, $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{OH}$, pale yellow prisms, m. p. 65—68° after slight previous softening, which is reduced by zinc dust in glacial acetic acid solution to *p*-methylthioltriphenylmethane, colourless needles, m. p. 68—69°. The carbinol is converted by hydrogen chloride in ethereal solution into *p*-methylthioltriphenylchloromethane, rhombic platelets, m. p. 88.5—89.5°, which undergoes a complicated decomposition when heated. The acid is converted by nascent bromine into *p*-methylsulphoxidetriphenylacetic acid, $\text{SOMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$, colourless, microscopic prisms, decomp. 130° (after four years the decomp. temperature had risen to 219—220°; the reason for this is unknown), and by potassium permanganate into *p*-methylsulphonetriphenylacetic acid, $\text{SO}_3\text{Me} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$, microscopic prisms, decomp. 140°. The

latter is transformed by concentrated sulphuric acid into *p*-methylsulphonetriphenylcarbinol, which appears to exist in two forms, m. p. 178–179° and 132° respectively; the former is produced when the latter is preserved, whilst the reverse change can occasionally be induced by crystallisation from a mixture of acetone and water.

Diphenyl- α -methylthiolnaphthylacetic acid, $\text{SMe} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$, rhombic leaflets, m. p. about 204° (decomp.) after previous darkening and softening, is prepared from benzoic acid and α -naphthylmethyl sulphide. (The sodium salt, needles, and methyl ester, colourless needles, m. p. 185–186°, are described.) It does not appear to be converted into the corresponding carbinol by treatment with sulphuric acid, although evolution of carbon dioxide occurs. When heated at 200–225°, it passes into *diphenyl- α -methylthiolnaphthylmethane*, $\text{CHPh}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{SMe}$, prisms, m. p. 157–158°.

Diphenyl sulphide can be condensed with benzoic acid, but the product has not been obtained in the crystalline condition.

The condensation of diphenyleneglycollic acid and anisyl mercaptan in boiling benzene solution in the presence of stannic chloride leads to the production of 9-*p*-methylthiolphenylfluorene, $\text{C}_6\text{H}_4 > \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{SMe}$, long needles, m. p. 126–128°. 9-*p*-Methyl-

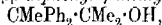
thiolphenylfluorene-9-carboxylic acid, $\text{C}_6\text{H}_4 > \text{C} < \begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{SMe} \\ \text{CO}_2\text{H} \end{smallmatrix}$, large, almost colourless leaflets, m. p. about 170° (decomp.), can, however, be obtained when diphenyleneglycollic acid and thioanisole react in glacial acetic acid solution in the presence of concentrated sulphuric acid at a temperature not exceeding 40–45°. Under the latter conditions, benzoic acid can be condensed with thiophenol, but investigation of the product is not complete. H. W.

Derivatives of Cinnamyl Alcohol and Phenylallyl Alcohol α -Phenylglycerol. CHARLES MOUREU and PATRICK GALLAGHER (*Bull. Soc. chim.*, 1921, [iv], 29, 1009–1017).—Phenylallyl alcohol or cinnamyl alcohol, when acted on by phosphorus tribromide or hydrogen bromide, gives in all cases the compound $\text{C}_6\text{H}_5 \cdot \text{C}_3\text{H}_5\text{Br}$ which has, in all probability, the constitution $\text{CHPh} \cdot \text{CH} \cdot \text{CH}_2\text{Br}$ (cf. Klages and Klenk, A., 1906, i, 638). This monobromo-derivative on bromination gives $\alpha\beta\gamma$ -tribromo- α -phenylpropane, which, when heated with silver acetate and acetic acid at 120–125° for thirty-five hours, gives *phenylglyceryl triacetate*, b. p. 175°/5–6 mm.: d_4^{20} 1.1871; n_D^{20} 1.4972. This triacetate, when boiled with dilute hydrochloric acid, yields α -phenylglycerol, b. p. 181°/4 mm.: d_4^{20} 1.2213; n_D^{20} 1.5605; n_D^{25} 1.5600; n_D^{30} 1.5593. W. G.

The Molecular Transposition accompanying the Dehydration of $\alpha\alpha$ -Diphenyl- $\beta\beta$ -dimethylpropan- α -ol. (MME) RAMART (*Compt. rend.*, 1921, 173, 1182–1184).—It has previously been shown that, when $\alpha\alpha$ -diphenyl- $\beta\beta$ -dimethylpropan- α -ol is dehydrated by means of a mixture of acetic anhydride and acetyl

chloride, a hydrocarbon and a chloro-compound, $C_{17}H_{19}Cl$, m. p. 109–110°, are obtained (cf. A., 1913, i, 1325). This chloro-compound yields with silver acetate a hydrocarbon, $C_{17}H_{18}$, and its constitution is now established as being $CH_3 \cdot CPh_2 \cdot CMe_2 \cdot Cl$.

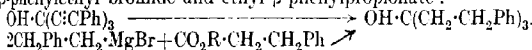
$\alpha\alpha$ -Diphenylpropaldehyde reacts with magnesium ethyl bromide to give $\beta\beta$ -diphenylpentan- γ -ol, b. p. 210–212°/40 mm., which by the action of thionyl chloride is converted into γ -chloro- $\beta\beta$ -diphenylpentane. Ethyl $\alpha\alpha$ -diphenylpropionate reacts with magnesium methyl iodide to give $\beta\beta$ -diphenyl- γ -methylbutan- γ -ol,



b. p. 186–187°/14 mm., which with thionyl chloride yields γ -chloro- $\beta\beta$ -diphenyl- γ -methylbutane, m. p. 108–109°, identical with the chloro-compound mentioned above. W. G.

Triphenylethynylcarbinol and its Analogues. KURT HESS and WILHELM WELTZIEN (*Ber.*, 1921, 54, [B], 2511–2521).—The authors have prepared and investigated triphenylethynylcarbinol, $OH \cdot C(C(CPh)_3)_2$, phenyldi-phenylethynyl-carbinol, $OH \cdot CPh(C(CPh)_2)_2$,

and diphenylphenylethynylcarbinol, $OH \cdot CPh_2 \cdot C(CPh)_2$, in order to ascertain if, as regards halochromy, these compounds resemble the carbinols including radicles of the triphenylmethyl type containing so-called tervalent carbon. The third of the above compounds is Nef's benzophenonephenylacetylene (A., 1900, i, 21) obtained by the action of sodium phenylacetylide on benzophenone, and the authors have prepared all three compounds by this method which gives, however, poor yields. Better results were obtained by the use of magnesium phenylethynyl bromide. That the reactions really proceed in the direction supposed and that, for instance (Kohler and Reimer, A., 1905, i, 347), in the action of magnesium phenylethylene bromide on phenylpropionic chloride the acetylene linking of the phenylpropionic acid does not participate, is shown by the fact that the action of hydrogen and platinum black in alcoholic solution converts the triphenylethynyl-carbinol into a compound obtainable also from magnesium β -phenylethyl bromide and ethyl β -phenylpropionate:



The action of magnesium phenylethynyl bromide on distyryl ketone yields a compound, $C_{25}H_{20}O$, which forms a yellow syrup solidifying to a deep brown, vitreous mass, gives a red solution with concentrated sulphuric acid, and has probably the constitution $Ph(C(C(OH)(CH_2CHPh)_2)_2$, although here also combination of phenylacetylene at an ethylene gap of the ketone is not excluded.

The three carbinols exhibit typical halochromy, and give respectively: (1) with concentrated sulphuric acid, bluish-violet, magenta, and orange-red solutions, (2) with perchloric acid, deep bluish-violet, Bordeaux, and orange-red precipitates, and (3) with stannic chloride, bright blue, Bordeaux, and reddish-violet precipitates. The colorations and precipitates are, however, so sensitive that no double compounds have yet been isolated. With

phenylacetylene or tolane, no sign of halochromy is revealed by the above reagents. The conclusion is drawn that the triphenylmethane configuration with its typical effects on the carbinol need not be attributed to the aromatic character of the benzene nucleus, since halochromy is observed when the benzene nuclei are replaced by "gap-linkings." Owing to the instability of these acetylene compounds, it was not found possible to replace the hydroxyl of the carbinols by halogens, so that the question of radicle-dissociation remains open.

Oxalyl chloride and magnesium phenylethynyl bromide react, giving a compound agreeing in composition with the formula $\text{OH}\cdot\text{C}(\text{C}\equiv\text{CPh})_2\cdot\text{C}(\text{C}\equiv\text{CPh})_2\cdot\text{OH}$, and an attempt is to be made to obtain by pinacone rearrangement a compound which, with magnesium phenylethynyl bromide, will yield an ethane derivative which contains only one hydroxyl group and may be examined for dissociation.

For the purpose of testing Gomberg's quinocarbonium theory, Schlenk and Ochs (A., 1915, i, 579) prepared tri-2-thionylcarbinol and regarded the halochromy of this compound as explainable by quinonoid rearrangement (cf. Pfeiffer and Böttler, A., 1919, i, 62). For triphenylethynylcarbinol, however, quinonoid rearrangement is excluded, unless a highly improbable allenic structure is assumed.

Tri-phenylethynyl-carbinol, $\text{C}_{25}\text{H}_{18}\text{O}$, prepared from magnesium phenylethynyl bromide and phenylpropionic chloride, crystallises in long, colourless needles, softening at 122° , m. p. $126-127^\circ$ (browning).

Phenyldiphenylethynylcarbinol, $\text{C}_{33}\text{H}_{24}\text{O}$, prepared from magnesium phenylethynyl bromide, ethyl bromide, magnesium, and phenylacetylene, forms a yellow oil.

Tri- β -phenylethylcarbinol, $\text{OH}\cdot\text{C}(\text{CH}_2\cdot\text{CH}_2\text{Ph})_3$, crystallises in bundles of long, colourless needles, softening at 66° , m. p. $68-69^\circ$.

The compound $\text{C}_{34}\text{H}_{22}\text{O}_2$ (see above), obtained from magnesium phenylethynyl bromide and oxalyl chloride, forms pale yellow crystals, softening at 128° , m. p. $130-131^\circ$ (decomp.). T. H. P.

Action of Nitrogen Iodide and of Cyanogen Iodide on Benзамidine. PAUL ROBIN (*Compt. rend.*, 1921, **173**, 1085-1086).—Nitrogen iodide readily reacts with benзамidine to give iodobenзамidine (A., 1920, i, 568), but cyanogen iodide gives a very unstable, additive compound, $\text{C}_7\text{H}_8\text{N}_2\cdot\text{CNI}$, m. p. 72° (decomp.). W. G.

Electrolytic Reduction of some Carboxylic Acids. HARUSHIGE INOUE (*J. Chem. Ind. Japan*, 1921, **24**, 906-918).—By the electrolytic reduction of (a) phenylacetic acid, (b) cinnamic acid, and (c) benzoic acid, the following substances were isolated in each case: (a) Phenylethyl alcohol and *r*- β -dihydroxy- α -diphenylbutane, m. p. 114.5° . (b) γ -Phenylpropyl alcohol and *r*- β -dihydroxy- α -diphenylhexane. (c) Benzyl alcohol. β - γ -Dihydroxy- α -phenyl- γ -methylbutane, m. p. 145° , was prepared by the same reducing method (cf. *J. Soc. Chem. Ind.*, 1922, Jan.). K. K.

The Electrochemical Oxidation of Aromatic Nitriles.

FR. FIGHTER and GUSTAV GRISARD (*Helv. Chim. Acta*, 1921, 4, 928—941).—The behaviour of benzonitrile, the three toluonitriles, phenylacetonitrile, and allied substances has been examined.

Benzonitrile is extensively degraded by electrochemical oxidation, in addition, hydroxylation of the nucleus takes place with the formation of catechol and 2:5-dihydroxybenzonitrile, colourless needles, m. p. 151°.

p-Toluenitrile is electrochemically oxidised at lead peroxide anodes with exceptional smoothness to *p*-cyanobenzoic acid; in the most favourable circumstances, the total yield of this substance and terephthalic acid amounts to 44.6%. *p*-Toluic acid, when dissolved in a mixture of acetone and sulphuric acid, is converted at a lead peroxide anode into terephthalic acid, the yield being 14%. In warm solution and with an excess of current, *p*-xylene is oxidised at a lead peroxide anode mainly to *p*-tolualdehyde, small quantities of *p*-toluic acid being also formed. From these results it is apparent that the electrochemical oxidation of the methyl to the carboxyl group is greatly facilitated by the presence of the cyano-radicle.

In a well-cooled solution, *o*-toluenitrile is converted at a lead peroxide anode into *o*-cyanobenzoic acid, the yield being 6.25%; in addition, very considerable degradation occurs. If the cooling is not efficient the nitrile becomes hydrolysed to *o*-toluic acid, which becomes oxidised to *o*-phthalic acid. *o*-Toluic acid is very extensively degraded in acetone-sulphuric acid solution at lead peroxide anodes; phthalic acid is formed to the extent of 5%.

m-Cyanobenzoic acid is produced in 28% yield from *m*-toluenitrile dissolved in a mixture of acetone and sulphuric acid at lead peroxide anodes; the formation of dark, resinous products is more marked in this case than with the other isomerides.

Under all conditions of electrochemical oxidation, phenylacetonitrile is attacked and suffers fission at the methylene group; the sole products are benzaldehyde and benzoic acid, which are also produced from phenylacetic acid.

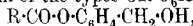
H. W.

Nitration, Chlorination, and Bromination of *m*-Hydroxybenzoic Acid. P. H. BEYER (*Rec. trav. chim.*, 1921, 40, 621—631).—On nitration *m*-hydroxybenzoic acid yields the 2-nitro-, 4-nitro-, and 6-nitro-derivatives together with a small quantity of a dinitro-acid (cf. Griess, A., 1887, 485). Chlorination yields the 2-chloro- and 6-chloro-acids (cf. Zincke and Walbaum, A., 1891, i, 708, and Mazzara, A., 1900, i, 596). Bromination, in acetic acid solution, yields the 4-bromo-derivative only (cf. Coppadoro, A., 1903, i, 257). For purposes of comparison with acids which other workers had stated to be obtainable by the methods used, but which were not so obtained, the following were prepared: 5-nitro-*o*-hydroxybenzoic acid, pale yellow crystals, m. p. 194—195°, was obtained by hydrolysis of the methyl ester prepared as described by Cohen and McCandlish from methyl 3:5-dinitrobenzoate (T.,

1905, **87**, 1266). Griess's 5-nitro-acid (A., 1887, 485) is in reality 6-nitro-*m*-hydroxybenzoic acid; 4-chloro-*m*-hydroxybenzoic acid, m. p. 219.5–220.5°, was obtained from 4-nitro-*m*-hydroxybenzoic acid by reduction, diazotisation, etc.; and 6-bromo-*m*-hydroxybenzoic acid, m. p. 185° (decomp.), was prepared similarly from 6-nitro-*m*-hydroxybenzoic acid.

H. J. E.

Some Derivatives of Saligenin. MERRILL C. HART and ARTHUR D. HIRSCHFELDER (*J. Amer. Chem. Soc.*, 1921, **43**, 1688–1693).—With a view to study their pharmacological properties derivatives of saligenin of the types $\text{OR}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$,



and $\text{R}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{O}\cdot\text{COR}$ were prepared. The ethers were prepared by heating potassium saligenate with the alkyl or aryl haloid on a water-bath under a reflux condenser. In this way, the authors obtained the ethyl ether, b. p. 264° (cf. Bötsch, A., 1882, 174), the propyl ether, b. p. 155–157°/24 mm.; the *n*-butyl ether, b. p. 160–162°/25 mm.; the isoamyl ether, b. p. 176°/27 mm., and the benzyl ether, b. p. 221–222°/25 mm., m. p. 37°.

The mono-esters were prepared by the action of acid chlorides or anhydrides on potassium saligenate in ether or alcoholic solutions. The monoacetate has b. p. 167–168°/29 mm.; the monobenzoate was a colourless oil; the dibenzoate obtained by benzylation in pyridine solution had m. p. 51°.

Potassium saligenate is best obtained by the action of alcoholic potassium hydroxide on saligenin in acetone solution. A good yield of 5-bromo-2-hydroxybenzyl alcohol was obtained by the method of Auwers and Büttner (A., 1899, i, 36). For the preparation of 5-iodo-2-hydroxybenzyl alcohol, Seidel's method (cf. A., 1899, i, 597) is not satisfactory. A good yield is obtained by treating saligenin in aqueous solution with a solution of iodine in aqueous potassium iodide.

W. G.

Complex Metallic Ammines. VI. *cis*-Phthalato-, *cis*-Homophthalato-, and other Diethylenediaminecobaltic Salts. JAMES COOPER DUFF (T., 1921, **119**, 1982–1988).

The Optically Active Forms of the Keto-dilactone of Benzophenone-2:4:2':4'-tetracarboxylic Acid. WILLIAM HOBSON MILLS and CHARLES REYNOLDS NODDER (T., 1921, **119**, 2094–2104).

Preparation of Vanillin from Acetylisoegenol. W. C. SIEVERS and L. GIVAUDAN AND CO. (Swiss Pat., 89053; from *Chem. Zentr.*, 1921, iv, 911).—Acetylisoegenol is oxidised in the presence of aromatic aminocarboxylic acids. For example, acetylisoegenol, as such, or dissolved in an appropriate solvent, is added to an aqueous solution of sodium dichromate. The mixture is mechanically shaken at 80° while a solution of *p*-aminobenzoic acid in 50% sulphuric acid is added. Acetylvainillin is extracted from the

products of reaction. The bisulphite compound is obtained and treated successively with acid and sodium hydroxide. G. W. R.

The Preparation of Aldehydes from Acid Chlorides. IV. Dialdehydes. I. KARL W. ROSENMUND, FRITZ ZETZSCHE, and CHR. FLÜTSCH (*Ber.*, 1921, 54, [B], 2888—2893).—An examination of the possibility of preparing di- and poly-aldehydes by the catalytic reduction of the corresponding acid chlorides (cf. A., 1918, i, 300; 1921, ii, 320).

The action is carried out by means of hydrogen in the presence of palladised kieselguhr in hot xylene solution, "sulphured" quinoline being used as regulator. Suberyl, isophthalyl, and terephthalyl chlorides are thus converted into the corresponding dialdehydes in 75—85% yield. *s-o*-Phthalyl chloride, on the other hand, gives mainly phthalide under these conditions; presumably the symmetrical is transformed into the unsymmetrical acid chloride by the palladium chloride formed during the reaction in the same manner as by aluminium chloride.

The following substances are described. Suberdialdehyde (dihemicarbazone, m. p. 183—185°, dioxime, m. p. 152°; *diphenylhydrazone*, colourless needles, m. p. 84—86°); *isophthalaldialdehyde*, m. p. 88—89°; *terephthalaldialdehyde*, m. p. 116°; *terephthalylidenedi- α -naphthylamine*, $C_{28}H_{20}N_2$, yellow crystals, m. p. 223—225° after softening at 210°; *terephthalaldialdehydedi-p-nitrophenylhydrazone*, crystalline powder, m. p. 281° (decomp.) after softening at 272°; *terephthalaldialdehydediphenylhydrazone*, yellow leaflets, m. p. 278° (decomp.) after softening at 265°.

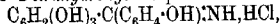
Terephthalyl chloride is converted by aniline in xylene solution into the *dianilide*, long, colourless needles, m. p. 334—337°, by α -naphthylamine into the *di- α -naphthalide*, needles, m. p. 334—335° (slight decomp.) after softening at 325°, and by diphenylamine into the *bisdiphenylamide*, colourless needles, m. p. 272—273° (decomp.) after softening at 268°. H. W.

The supposed True Dibenzoylmethane of Wislicenus; New Experiments. CHARLES DUFRAISSE and PIERRE GÉRALD (*Compt. rend.*, 1921, 173, 985—987).—It has been shown previously (A., 1921, i, 114) that the compound obtained by Wislicenus by the saponification of phenyl bromostyryl ketone with alcoholic sodium hydroxide is not dibenzoylmethane, $(CH_2(COPh)_2)$, and evidence is now produced to show that the compound is really α -benzoyl- β -ethoxy- β -phenylethylene, $COPh \cdot CH \cdot CPh \cdot OEt$.

Benzoylphenylacetylene readily condenses with ethyl alcohol (cf. Moureu and Brachin, A., 1904, i, 811) to give a compound which is identical with Wislicenus's compound. Wislicenus's reaction really takes place in two stages. In the first stage, a molecule of ethyl alcohol is added at the double linking, giving α -bromo- α -benzoyl- β -ethoxy- β -phenylethane, $COPh \cdot CHBr \cdot CPh \cdot OEt$, m. p. 60—61°; b. p. 182—183°/3—4 mm., which then loses a molecule of hydrogen bromide, giving Wislicenus's compound.

W. G.

Hydroxycarbonyl Compounds. 2:4:6:2'-Tetrahydroxybenzophenone. P. KARRER (*Helv. Chim. Acta*, 1921, 4, 992—993).—2:4:6:2'-Tetrahydroxybenzophenoneketimide hydrochloride,



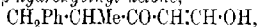
colourless needles, separates gradually when a solution of salicylonitrile and phloroglucinol in anhydrous ether is saturated with hydrogen chloride in the presence of anhydrous zinc chloride and preserved at the atmospheric temperature during several days; it is a relatively stable substance which may be crystallised from fuming hydrochloric acid. It is hydrolysed by hot water to 2:4:6:2'-tetrahydroxybenzophenone, $\text{C}_6\text{H}_2(\text{OH})_3\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, yellow leaflets which gradually decompose and blacken when heated; the latter has marked anti-diarrhoeic action. H. W.

The Products of the Reduction of Hydroxymethyleneacetophenone [Phenyl β -Hydroxyvinyl Ketone] and of α -Hydroxymethylene- α -benzylacetone [β -Phenyl- α -hydroxymethylene-ethyl Methyl Ketone]. HANS RUPE and HANS MÜLLER (*Helv. Chim. Acta*, 1921, 4, 841—860).—The successful reduction of hydroxymethylenecamphor to camphylcarbinol by hydrogen in the presence of nickel has led the authors to investigate the behaviour of phenyl β -hydroxyvinyl ketone and β -phenyl- α -hydroxymethylene-ethyl methyl ketone under similar conditions; the reactions in these cases are found to follow a complex course.

Phenyl β -hydroxyvinyl ketone, $\text{COPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$, is not smoothly reduced by hydrogen in the presence of nickel in aqueous-alcoholic solution. Its reduction by aluminium amalgam in moist ethereal solution, and the action of nickel and hydrogen, sodium amalgam, and zinc dust and ammonium chloride respectively on its sodio-compound, are described fully. Apart from the formation of very considerable amounts of resinous by-products, hydrogenation proceeds in such a manner that the double bond and the ketonic group are affected simultaneously, giving the corresponding glycol, which passes by loss of water into the unsaturated secondary alcohol, thus: $\text{COPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH} + 2\text{H}_2 = \text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{OH}\cdot\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2$. α -Dihydroxy- α -phenylpropane is a colourless, odourless liquid, b. p. 175°/11 mm. (slight decomp.). It is smoothly transformed by benzoyl chloride in the presence of pyridine into the corresponding dibenzoate, colourless needles, m. p. 51°, which loses benzoic acid when heated and passes into cinnamyl benzoate, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OBz}$, a highly refractive liquid, b. p. 209°/13 mm. α -Phenylallyl alcohol, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2$, is a colourless liquid, b. p. 92°/11 mm., 214°/760 mm., the constitution of which is proved by its conversion, by means of ozone, into mandelic acid. The corresponding benzoate, a colourless, mobile liquid, has b. p. 182°/12 mm.

The reduction of styryl methyl ketone to β -phenylethyl methyl ketone, b. p. 112—113°/12 mm., is effected with unusual ease and in 98—100% yield by means of hydrogen and nickel. The condensation of the saturated ketone with ethyl formate in the presence of sodium, sodamide, or sodium ethoxide is described

fully, the latter agent being preferentially used, since it leads to the production of the α -compound (yield 80%) and γ -compound (yield 10—15%) which are separated by taking advantage of the solubility of the copper salt of the latter in cold benzene in which the copper compound of the former does not dissolve. β -Phenyl- α -hydroxymethylene-ethyl methyl ketone, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{CH}\cdot\text{OH})\cdot\text{COMe}$, is an extremely unstable substance characterised by the readiness with which it passes into β -acetylindene (see later) when heated or, more particularly, when treated with a trace of acid; the corresponding sodium salt, a pale yellow, amorphous powder, copper salt, steel-blue leaflets, m. p. 184° , and amorphous nickel salt are described. The sodium salt is readily converted in aqueous solution by the addition of the hydrochloride of the requisite base into the *imide*, $\text{CH}_2\text{Ph}\cdot\text{CAc}\cdot\text{CH}\cdot\text{NHPh}$, lemon-yellow needles, m. p. 130 — 134° (indefinite), and *p-toluidide*, pale yellow needles, m. p. 103° . The corresponding *amide* crystallises in long, almost colourless needles, m. p. 95° . The *benzoate*, triclinic crystals, m. p. 73° , is most conveniently prepared from benzoyl chloride and the copper salt in well-cooled pyridine solution. By reason of its instability, the reduction of β -phenyl- α -hydroxymethylene-ethyl methyl ketone appears to be impossible, but the benzoate is readily hydrogenated in accordance with the scheme: $\text{CH}_2\text{Ph}\cdot\text{CAc}\cdot\text{CH}\cdot\text{OBz} + \text{H}_2 \rightarrow \text{CH}_2\text{Ph}\cdot\text{CHAc}\cdot\text{CH}_2\cdot\text{OBz} \rightarrow \text{CH}_2\text{Ph}\cdot\text{CAc}\cdot\text{CH}_2 + \text{Ph}\cdot\text{CO}_2\text{H} \xrightarrow{+\text{H}_2} \text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{COMe}$. α -Phenylisopropylethyl methyl ketone, b. p. 118 — $120^\circ/14$ mm., gives a *semicarbazone*, colourless needles, m. p. 112° ; it is converted by ethyl formate and sodium ethoxide into α -phenylisopropyl β -hydroxyvinyl ketone,



slender, colourless needles, m. p. 62° (the sodium, nickel, and copper salts are described).

β -Acetylindene, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_3 \\ \text{CH} \end{smallmatrix}\rangle\text{CAc}$, asbestos-like needles, m. p. 123° (*phenylhydrazone*, colourless needles, m. p. 225°) is most conveniently prepared from β -phenyl- α -hydroxymethylene-ethyl methyl ketone by the action of hydrochloric or formic acid. It is converted by concentrated nitric acid or ozone into phthalic acid; the isolation of an intermediate compound could not be effected.

β -Phenylethyl β -hydroxyvinyl ketone, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$ (see above), crystallises in colourless needles, m. p. 99° , b. p. 139 — $140^\circ/12$ mm. It is moderately stable when pure and dry, but is rapidly and quantitatively decomposed by traces of mineral acids into formic acid and β -phenylethyl methyl ketone. The sodium and copper salts and the *benzoate*, colourless needles, m. p. 99 — 100° , are described. H. W.

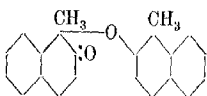
Additive Reactions of the Carbonyl Group involving the increase in Valency of a Single Atom. JAMES B. CONANT *J. Amer. Chem. Soc.*, 1921, **43**, 1705—1714, 2125: cf. preceding abstracts.—The additive reactions of the phosphorus haloids with carbonyl compounds are of a different type from the reactions of

most reagents with these compounds in that they involve the formation of a cyclic compound and the increase in valency of a single phosphorus atom. The reaction is reversible and is analogous to reactions such as the addition of halogen acids to ammonia. The author has applied Lewis's theory of the cubical atom (cf. A., 1916, ii, 310) to this problem. He considers that the positive nucleus of the carbon atom of the carbonyl group is exposed by the drawing away of the electrons of the double bond, and that the exposed nucleus behaves, in additive reactions, like a positively charged atom and unites with atoms having unshared electrons. Such an atom is the phosphorus atom in phosphorus trichloride and the nitrogen atom in ammonia. The resulting additive compounds may undergo various irreversible intramolecular changes or react irreversibly with other reagents giving stable products.

Phosphorus tribromide combines with phenyl styryl ketone in the 1:4-position, the reaction being parallel to that with the trichloride and the equilibrium has been determined in each case. It is more in favour of the additive product in the case of the tribromide than with the trichloride. W. G.

1:2-Naphthaquinols. K. FRIES (*Ber.*, 1921, **54**, [B], 2925—2930).—The compound described by Fries and Hübner (A., 1906, i, 190) as 1:2-naphthamethylenequinone, $C_6H_4 \begin{smallmatrix} C(CH_3)_2 \cdot CO \\ CH=CH \end{smallmatrix}$

has been shown by Pummerer and Cherbuliez (A., 1915, i, 418; 1919, i, 440) to have the constitution indicated by the annexed formula and to be dissociable in solution into 1:2-naphthamethylenequinone and 1-methyl- β -naphthol. They have therefore considered that the dehydro-com-



pound obtained from 6-bromo-1-methyl- β -naphthol (Fries and Hübner, *loc. cit.*) must yield 6-bromo-1-methyl- β -naphthyl acetate (in addition to the compound, $C_{13}H_{10}O_2ClBr$, previously isolated) when acted on by acetyl chloride; this is now shown to be the case.

It is also shown that the constitution, $C_6H_3Br \begin{smallmatrix} C(CH_3)_2 \cdot COAc \\ CH=CH \end{smallmatrix}$,

assigned previously to the compound $C_{13}H_{10}O_2ClBr$, is incorrect, since it is hydrolysed to 4-chloro-6-bromo-1-methyl- β -naphthol, needles, m. p. 179°, and hence must be 4-chloro-6-bromo-1-methyl- β -naphthyl acetate. The course of the reaction is explained by the fission of dehydro-6-bromo-1-methyl- β -naphthol into the quinol chloride, $C_6H_3Br \begin{smallmatrix} CMeCl \cdot CO \\ CH=CH \end{smallmatrix}$, which is converted into the

acetate of 4-chloro-6-bromo-1-methyl- β -naphthol and 6-bromo-1-methyl- β -naphthol which becomes acetylated.

The following new compounds are described. 4-Chloro-1-methyl- β -naphthol, colourless needles, m. p. 101°, and its acetate, lustrous prisms, m. p. 78°; the compound, $C_6H_3Br \begin{smallmatrix} CMe(NO_2) \cdot CO \\ CCl=CH \end{smallmatrix}$, small

prisms, m. p. 127° (decomp.); 1 : 3 : 4 : 4-tetrachloro-2-keto-1-methyl-tetrahydronaphthalene, $\text{C}_6\text{H}_3\text{Cl}_4$ $\begin{array}{c} \text{CMeCl} \cdot \text{CO} \\ | \\ \text{CCl}_2 - \text{CHCl} \end{array}$, prisms, m. p. 82°.

H. W.

Oxidation and Reduction of Quinol and Quinone from the Point of View of Electromotive Force Measurements. F. S. GRANGER and J. M. NELSON (*J. Amer. Chem. Soc.*, 1921, **43**, 1401—1415).—The reaction $\text{C}_6\text{H}_4\text{O}_2 \rightleftharpoons \text{C}_6\text{H}_4\text{O} + 2\text{H} + 2\ominus$ has been investigated by measurement of the *E.M.F.* of solutions of quinone, quinol, and quinhydrone in water and hydrochloric acid by means of combinations of the type $\text{Hg} | \text{HgCl} (\text{sat.}) | \text{KCl} | \text{KCl} (\text{sat.}) | \text{Solution of } \text{C}_6\text{H}_4\text{O}_2 \text{ and } \text{C}_6\text{H}_4\text{O}_2 \text{ in HCl} | \text{Pt}$. In addition to the *E.M.F.* data, values for the solubility of the constituents in water and hydrochloric acid are required and were obtained. The solubility of quinol at 25° is found to be (a) in water 0.645 mol. per litre, (b) in 0.01*N*-hydrochloric acid, 0.645 mol. per litre, (c) in 0.1*N*-hydrochloric acid, 0.633 mol. per litre, and (d) in *N*-hydrochloric acid, .494 mol. per litre. The solubility of quinone at 25° in water is .1266 mol. per litre, in 0.1*N*-hydrochloric acid 0.1275 mol. per litre, and in *N*-hydrochloric acid 0.1332 mol. per litre. The solubility of quinhydrone in the presence of one another has been determined and the dissociation constant (*K*) of quinhydrone calculated. The value of *K* in water is 0.289, in 0.1*N*-hydrochloric acid 0.263, and in *N*-hydrochloric acid 0.267. Several tables of potential measurements are given, and these values are compared with calculated values and found to be in fair agreement. The equilibrium constant (*k*) for the reaction quinol \rightleftharpoons quinone is calculated by means of the equation $\pi = 0.0298 \log q/h + 0.0596 \log (\text{H}^+) - 0.0298 \log k$, and the value 1.6×10^{-23} obtained. J. F. S.

The Dibromoanthraquinones. MARTIN BATTEGAY and J. CLAUDIN (*Bull. Soc. chim.*, 1921, [iv], **29**, 1017—1027; cf. Grandmougin, A., 1921, i, 871).—A more detailed account of work already published (A., 1921, i, 349). 1 : 6-Dibromoanthraquinone, m. p. 204°, is obtained by heating 1-nitro-6-sulphoanthraquinone with bromine in a sealed tube for eight hours at 210°. 1 : 7-Dibromoanthraquinone, m. p. 220°, is obtained in the same manner from 1-nitro-7-sulphoanthraquinone, or from 1 : 7-diaminoanthraquinone by the Sandmeyer reaction. W. G.

The Homonuclear Dibromoanthraquinones. E. GRANDMOUGIN (*Compt. rend.*, 1921, **173**, 839—840; cf. A., 1921, i, 871). Very scanty details are given for the preparation of the four homonuclear dibromoanthraquinones, namely, the 1 : 2-, 1 : 3-, 1 : 4-, and 2 : 3-derivatives. W. G.

The Dibenzooyldiaminoanthraquinones. MARTIN BATTEGAY and J. CLAUDIN (*Bull. Soc. chim.*, 1921, [iv], **29**, 1027—1036).—A part a more detailed account of work already published (cf. A., 1921, i, 513). 1 : 2- and 2 : 3-Diaminoanthraquinones when

benzoylated in neutral or acid media give the corresponding 2-phenyl-anthraquinoneiminazole, but in alkaline solution the benzoylation yields the dibenzoyl derivative. 2-Phenyl-*x*-anthraquinoneiminazole, m. p. 235° (Schaarschmidt, A., 1915, i, 177 gives m. p. 271°), in an alkaline vat dyes cotton an orange-yellow, which passes by oxidation to a very fast, intense bright yellow. 1:2-Dibenzoyl-diaminoanthraquinone has m. p. 355°. 2-Phenyl-*β*-anthraquinoneiminazole has m. p. >360° (Schaarschmidt, loc. cit., gives >385°), and 2:3-dibenzoyldiaminoanthraquinone has m. p. 315°. 2:6-Dibenzoyldiaminoanthraquinone has m. p. 300°, and 2:7-dibenzoyldiaminoanthraquinone has m. p. 300°. Of these dibenzoyl derivatives only the 1:4-, 1:5-, and 1:8-derivatives are powerful dyes.

W. G.

The Intermediate Products in the Synthesis of Alizarin. EUGÈNE GRANDMOUGIN (*Compt. rend.*, 1921, **173**, 1176—1178; cf. A., 1921, i, 871).—The author considers that the stages in the synthesis of alizarin from anthracene are: anthracene → 10-dibromoanthracene → its tetrabromide → 2:3:9:10-tetrabromoanthracene → 2:3-dibromoanthraquinone → alizarin.

W. G.

Derivatives of *l*-Menthol. E. A. LÜCK (*Apoth.-Zeit.*, 1921, **36**, 279; from *Chem. Zentr.*, 1921, iii, 721).—The following derivatives of *l*-menthol are described: cyanomenthane, C₁₁H₁₉N, yellowish-white needles; potassium menthancarboxylate, C₁₁H₁₉O₂K, long, yellow needles; menthancarboxylic acid, C₁₁H₂₀O₂, white needles; menthinaldehyde corresponding with the latter acid, C₁₁H₂₀O, silky needles; the secondary alcohol from the aldehyde, C₂₂H₄₀O₂, slender, white needles; the ketone, C₂₂H₃₈O₂, white needles; sesquiterpene from menthone, C₁₅H₂₄ or C₃₀H₄₈, brownish-black, thick mass, not solidifying after two months; nitroso-sesquiterpene, C₃₀H₄₇NO, a light yellow syrup; the compound, CSSK-C₃₀H₄₅NO·OK, yellow needles, detonating on heating.

G. W. R.

Essential Oil of *Nepeta japonica*, Maxim. I. YOSHIHARU MURAYAMA and TAKEYOSHI ITAGAKI (*J. Pharm. Soc. Japan*, 1921, 869—880).—An essential oil (1.8%) was obtained by steam distillation of *Nepeta japonica*, Maxim, from China. It boils at about 205° or 63—83°/10 mm. and contains *d*-limonene and a small quantity of free acids, esters, and alcohols, but consists mainly of a ketone, C₁₀H₁₈O, which seems to be *d*-menthone, the optical antipode of the common *l*-menthone.

K. K.

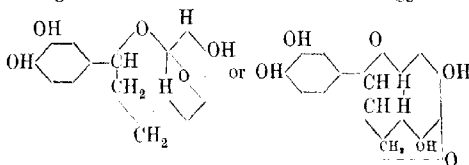
The Essential Oils of *Leptospermum flavescens* var *grandiflorum* and *Leptospermum odoratum*. A. R. PENFOLD (*J. Roy. Soc. New South Wales*, 1920, **54**, 197—207; cf. A., 1921 i, 859).—The chief constituents of the essential oil of *Leptospermum flavescens* var. *grandiflorum* are the two sesquiterpenes aromadendrene and eudesmene, together with a sesquiterpene alcohol not identified. The oil has d_{20}^{25} 0.9324; $[\alpha]_D$ -2.42°; n_D^{20} 1.5048 and is

distinct from the oil of *Leptospermum flavescens*. The principal constituents of the essential oil of *Leptospermum odoratum*, Cheel, are eudesmol, aromadendrene, and eudesmene, β -pinene, α -pinene, the butyric and acetic esters of an unknown alcohol, together with a small amount of an alcohol having an odour of citronellol, but not being either geraniol or citronellol, and small amounts of a solid and liquid phenol. The yield of oil was much higher from leaves cut in August or October than from those cut in May, and the eudesmol was present in minimum amount in the latter oil.

W. G.

The Structural Formula of Caoutchouc according to Harries. S. C. J. OLIVIER (*Rec. trav. chim.*, 1921, **40**, 665—676; cf. Harries, A., 1904, j, 757, and 1905, i, 364).—The author has repeated some of Harries's work and has obtained, in some cases, different results. He concludes that the assumption of homogeneity for the ozonide of caoutchouc is not valid and that the molecular weight cannot serve as a basis for estimating that of caoutchouc itself; further, that it is impossible in the present state of our knowledge to choose between the ring formula suggested by Harries and the Weber open-chain formula. H. J. E.

Catechu and Catechin. ASTRID CLEVE VON EULER (*Svensk. Kem. Tidskr.*, 1921, **33**, 88—98; from *Chem. Zentr.*, 1921, iii, 731).—A theoretical discussion of the chemistry of catechu and catechin. From a consideration of existing experimental work, the following alternative formulae for catechin are suggested:



G. W. R.

The Course of the Reaction in the Synthesis of Oxindigo 2:2'-Diketo- Δ^{11} -dicoumaran]. K. FRIES and H. HASENJÄGER (*Ber.*, 1921, **54**, [B], 2931—2934; cf. Fries and Hasselbach, A., 911, i, 150).—When 6-methyl-3-coumaranone reacts with 3-keto-2-*p*-dimethylaminoanilicoumaran in xylene solution, 2'-*p*-dimethylaminoanilino-6-methyl-2 : 2'-dicoumaranone, brownish-red, glistening needles, m. p. 232° (decomp.), after sintering at 229°, is obtained. It is hydrolysed by strong acids to *p*-aminodimethylaniline and "6-methyloxindigo." 3-Keto-2-*p*-dimethylaminoanil-6-methylcoumaran and 3-coumaranone, on the other hand, yield the isomeric 2-*p*-dimethylaminoanilino-6-methyl-2 : 2'-dicoumaranone, pale brownish-red needles, m. p. 211° (decomp.), after sintering at 208°. It is hydrolysed by strong acids to *p*-aminodimethylaniline and "6-methyloxindigo."

2 : 2'-Diketo-6-methyl- Δ^{11} -dicoumaran ("6-methyloxindigo," "6-methyl-2 : 2'-dicoumaranone-indigo"), crystallises from glacial acetic acid in small, yellow, prismatic crystals, m. p. 265° (decomp.), after darkening at 220° and sintering at 240° .

It follows, therefore, that the isomeric 2- or 2'-*p*-dimethylamino-anilino-6-methyl-2 : 2'-dicoumaranones are the primary reaction products and not "6-methyloxindigo." F. M. R.

Syntheses in the Thianthren Series. I. JÑANENDRA NATH RAY (T., 1921, 119, 1959-1967).

Preparation of Nitrosulphonic Acids of Hydrogenated Cinchona Alkaloids. C. F. BOEHRINGER & SÖHNE (D.R.P. 338738; from *Chem. Zentr.*, 1921, iv, 709-710).—Nitrosulphonic acids are prepared by dissolving hydrogenated cinchona alkaloids or their salts in a mixture of sulphuric and nitric acids, or nitric acid or an alkali nitrate is added to a solution of them in sulphuric acid, or their nitro-compounds are dissolved in strong sulphuric acid. *Nitrohydrocinchonidinesulphonic acid*, $C_{19}H_{23}O_6N_3S$, forms yellow, microscopic crystals; hexagonal plates are obtained from methyl alcohol; it is decomposed by heating with hydrochloric acid, giving *nitrohydrocinchonidine* and sulphuric acid. It chars without melting. *Nitrohydroquininesulphonic acid*, $C_{20}H_{25}O_6N_3S$, forms yellow needles; it chars without melting on heating above 250° and darkens on exposure to light. By heating with hydrochloric acid, sulphuric acid and *nitrohydroquinine* are obtained. The latter forms thin, yellow leaflets, m. p. 212° (decomp.). *Nitroethylhydrocupreinesulphonic acid*, $C_{21}H_{27}O_6N_3S$, forms yellow crystals which darken at about 260° and char at about 280° without melting. It is decomposed on heating with hydrochloric acid into sulphuric acid and *nitroethylhydrocupreine*. G. W. R.

Preparation of Aminosulphonic Acids of Hydrogenated Cinchona Alkaloids. C. F. BOEHRINGER & SÖHNE (D.R.P. 339947; from *Chem. Zentr.*, 1921, iv, 912).—Nitrosulphonic acids, derived from hydrogenated cinchona alkaloids, are reduced by means of ferrous sulphate and alkali hydroxide. For example, nitrohydroquininesulphonic acid is reduced by ferrous sulphate in the presence of an aqueous or methyl-alcoholic solution of barium hydroxide to *aminohydroquininesulphonic acid*; it forms yellow needles, m. p. $222-224^{\circ}$. The red crystalline sulphate gives *aminohydroquinine*, m. p. $216-218^{\circ}$, by hydrolysis with strong hydrochloric acid. G. W. R.

Preparation of Acetylsalicylyl Compounds of Quinine and its Derivatives. E. MERCK, CLAUD DIEHL, and HANS MAYEN (D.R.P. 338853; from *Chem. Zentr.*, 1921, iv, 709).—*o*-Acetoxybenzoyl chloride is allowed to react with molecular proportions of quinine or its derivatives in a suitable solvent. By the action of *o*-acetoxybenzoyl chloride on dry quinine in dry alcohol, *o*-acetoxybenzoyl-quinine hydrochloride is obtained in white needles or plates, m. p. 242° (decomp.). From a solution of ethylhydrocupreine in dry

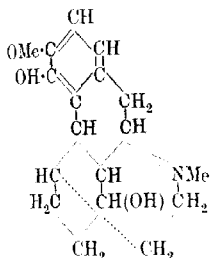
toluene, *o*-acetoxybenzoyl ethylhydrocupreine hydrochloride is similarly prepared; it forms white needles, m. p. 252° (decomp.).

G. W. R.

The Active Constituent of Ergot. K. SPIRO and A. STOLL (*Verh. Schweiz. Nat. Ges.*, 1920, reprint; from *Chem. Zentr.*, 1921, iii, 889—890).—Ergotamine, obtained in crystallisable form from ergot, on treatment with methyl alcohol gives a new, less active, alkaloid, *ergotaminine*. Ergotamine acts paralytically on the sympathetic system, causes contraction of plain muscular tissue, and a slight decrease in blood pressure. It acts on the uterus even at great dilutions. Ergotaminine exerts a similar effect. Histamine takes no part in the typical ergot effect. Ergotamine, however, acts similarly to ergot and may be used in the same way.

G. W. R.

Hydrogenation of isoCodeine and ψ -Codeine. EDMUND SPEYER and HERMANN WIETERS (*Ber.*, 1921, 54, [B], 2647—2650).—Catalytic hydrogenation in the presence of palladium proceeds differently in the cases of isocodeine and ψ -codeine, since the former is transformed into a dihydro-derivative, whereas the latter gives tetrahydro- ψ -codeine to which, on the basis of Knorr's formula for ψ -codeine, the annexed configuration is assigned.



Dihydroisocodeine, $C_{18}H_{23}O_3N$, crystallises in small, rhombic prisms, m. p. $199-200^{\circ}$; the corresponding *picrate*, m. p. $235-237^{\circ}$, after previous softening, the *hydrochloride* and *hydroiodide* are described. The *methiodide* forms leaflets, m. p. 272° . *Tetrahydro- ψ -codeine*, $C_{18}H_{25}O_3N \cdot 0.5H_2O$, crystallises in rhombic prisms, m. p. $114-115^{\circ}$ after softening at 110° ; it dissolves in solutions of alkali hydroxides from which it is precipitated by ammonium chloride. The *hydrochloride*, microscopic prisms, m. p. $238-240^{\circ}$ (decomp.), and *methiodide*, prisms, m. p. $249-250^{\circ}$ (decomp.), are described.

H. W.

Constitution of Rutaecarpine. YASUHIKO ASAHINA and ATSUSHI FUJITA (*J. Pharm. Soc. Japan*, 1921, 863—869).—Asahina and Mayeda (cf. A., 1916, i, 238, 621; A., 1921, i, 48) proposed constitutional formulae for evodiamine and rutaecarpine, alkaloids isolated from the fruits of *Evodia rutaecarpa*, Benth. and Hook. The authors attempted to reduce rutaecarpine with alcohol and sodium, with hydriodic acid, with zinc amalgam and hydrochloric acid, and with acetic acid and sodium amalgam in methyl-alcoholic solution without obtaining any definite compound except rutaecarpine hydroiodide, m. p. 270° . When rutaecarpine was heated with amyl alcohol and potassium hydroxide for two hours, anthranilic acid and 2-3-aminoethylindole-3-carboxylic acid, $C_{11}H_{12}O_2N_2$, were isolated in almost quantitative amount. The acid forms

white, silky crystals, m. p. 257° , is almost insoluble in common organic solvents, but soluble in acetic acid and hot dilute alcohol; yields a *picrate*, orange-yellow scales, m. p. 247° (decomp.), and when boiled with dilute hydrochloric acid for two to three hours, is resolved into 2- β -aminoethylindole and carbon dioxide. This confirms the constitution previously suggested for rutaccarpine.

K. K.

The Addition of Organic Bases to Metallic Salts. WALTER PETERS (*Z. anorg. Chem.*, 1921, **118**, 172—176).—It was shown in previous papers (A., 1913, ii, 42; 1915, i, 504) that by the addition of ammonia or amines to complex salts, compounds of much higher co-ordination number were obtained than by the addition of ammonia to simple salts. The work has now been extended by the preparation of a number of pyridine, piperidine, and ethylenediamine additive compounds of double platino- and platinum-chlorides. No relation was found between the number of molecules of each base combined with a salt and the affinity or dissociation constant of the base. The following compounds were prepared.

Pyridine compounds: $\text{CuPtCl}_6 \cdot 6\text{C}_5\text{H}_5\text{N}$, long, thick, cornflower-blue needles; $\text{CdPtCl}_6 \cdot 6\text{C}_5\text{H}_5\text{N}$, a white, curdy precipitate by adding pyridine to the aqueous solution of the salt;

$\text{MnPtCl}_6 \cdot 6\text{C}_5\text{H}_5\text{N}$,

a brick-red precipitate changing to brown; $\text{NiPtCl}_6 \cdot 6\text{C}_5\text{H}_5\text{N}$, yellowish-green; $\text{CoPtCl}_6 \cdot 6\text{C}_5\text{H}_5\text{N}$, yellowish-brown.

Piperidine compounds: $\text{Na}_2\text{PtCl}_4 \cdot 2\text{C}_5\text{H}_{11}\text{N}$, reddish-brown precipitate; $\text{BaPtCl}_4 \cdot 4\text{C}_5\text{H}_{11}\text{N}$; $\text{Na}_3\text{PtCl}_6 \cdot 4\text{C}_5\text{H}_{11}\text{N}$, pale yellow crystals; $\text{CuPtCl}_6 \cdot 2\text{C}_5\text{H}_{11}\text{N}$, greenish-blue precipitate;

$\text{ZnPtCl}_6 \cdot 4\text{C}_5\text{H}_{11}\text{N}$,

white; $\text{CdPtCl}_6 \cdot 2\text{C}_5\text{H}_{11}\text{N}$, olive; $\text{NiPtCl}_6 \cdot 6\text{C}_5\text{H}_{11}\text{N}$, dirty green.

Ethylenediamine compounds: $\text{ZnPtCl}_6 \cdot 2\text{C}_2\text{H}_4(\text{NH}_2)_2$, white; $\text{CdPtCl}_6 \cdot 6\text{C}_2\text{H}_4(\text{NH}_2)_2$, small crystals with a yellow tinge; $\text{NiPtCl}_6 \cdot 2\text{C}_2\text{H}_4(\text{NH}_2)_2$, bright red.

E. H. R.

Action of Sodammonium on Pyridine. Preparation of the Hydrate of Tetrahydroadipyrindyl. P. LEBEAU and M. PRON (*Compt. rend.*, 1921, **173**, 1178—1180).—When pyridine, cooled to -60° , is allowed to drop slowly on to sodammonium, a compound, $(\text{C}_5\text{H}_5\text{NNa})_2\text{NH}_3$, is obtained which retains its ammonia even in a vacuum. This compound is spontaneously inflammable in air and detonates. It reacts with methyl and propyl iodides, *tert*-amyl chloride, and ethylene dichloride giving in all cases unstable substances. By the controlled action of alcohol and water in the presence of ether, *tetrahydroadipyrindyl hydrate*, $(\text{C}_5\text{H}_6\text{N})_2\text{H}_2\text{O}$, is obtained from which the corresponding *hydrochloride*,

$(\text{C}_5\text{H}_6\text{N})_2\text{HCl}$,

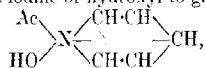
and *mercurichloride*, $(\text{C}_5\text{H}_6\text{N})_2\text{HCl} \cdot \text{HgCl}_2$, were prepared. W. G.

Reduction of Pyridine with Zinc Dust and Acetic Anhydride. OTTO DIMBOTH and RICHARD HEENE (*Ber.*, 1921, **54**, [B], 2934—2942).—Pyridine is readily reduced by zinc dust in the presence of acetic anhydride to 1:1'-*diacetyltetrahydro-4:4'-dipyridyl*,

$\text{AcN} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \end{smallmatrix} \text{CH} \cdot \text{CH} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \end{smallmatrix} \text{NAc}$, long, yellow needles, m. p. 124–125°, which on exposure to moist air is converted gradually into 4:4'-dipyridyl and acetic acid. De-acetylation and oxidation to 4:4'-dipyridyl is also observed by the action of manganese dioxide or lead dioxide on the substance dissolved in acetic acid or by the action of air or nitrous fumes on the alcoholic solution. It is transformed by iodine in benzene solution to 4:4'-dipyridyl, but pyridine is the main product of the action of iodine dissolved in potassium iodide on a solution of the acetyl compound in acetic acid. Conversely, 4:4'-dipyridyl is reduced by zinc dust and acetic anhydride to 1:1'-diacetyltetrahydro-4:4'-dipyridyl. The relationships are thus similar to those observed by Emmert between pyridine and tetrahydrodipyridyl (A., 1919, i, 415; 1920, i, 331). Like the dialkyl compound, 1:1'-diacetyltetrahydro-4:4'-dipyridyl undergoes dissociation into radicals; the solution of the substance in glacial acetic acid becomes intensely blue when gently warmed, but is decolorised by air and the alternate coloration and decolorisation can be repeated until the substance is completely oxidised. It appears that the radicle can react in two forms, $\text{NAc} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \end{smallmatrix} \text{C} < \text{H}$

and $\begin{smallmatrix} \text{Ac} & & \text{CH} \cdot \text{CH} \\ & \diagdown \quad \diagup & \\ & \text{N} & \\ & \diagup \quad \diagdown & \\ & \text{CH} \cdot \text{CH} & \end{smallmatrix} \text{CH}$. The first form gives a peroxide,

$\text{NAc} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \end{smallmatrix} \text{CH} \cdot \text{O} \cdot \text{O} \cdot \text{CH} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \end{smallmatrix} \text{NAc}$, with air which, possibly after transformation into $\text{NAc} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \end{smallmatrix} \text{C} < \text{OH}$, loses acetic acid, whereupon two residues unite to form 4:4'-dipyridyl. The second form adds iodine or hydroxyl to give



which loses acetic acid and yields pyridine.

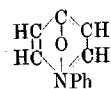
Diacetyltetrahydrodipyridyl can also be obtained in a colourless modification when the yellow variety is warmed with alcoholic potassium hydroxide solution (the acetyl groups are remarkably stable towards this reagent). Since the yellow and colourless forms are chemically indistinguishable and have the same melting point, it would appear at first sight that the coloured crystals are contaminated by some persistent, coloured impurity. Against this view, however, it is observed that the solution of the colourless compound in acetic anhydride becomes yellow when warmed and deposits yellow crystals when subsequently cooled. The yellow compound deposits a small quantity of orange-red needles, m. p. (indefinite) 248°, when warmed with a small quantity of acetic acid or acetic anhydride; the substance has not yet been investigated completely.

Quinoline, also, is readily reduced by zinc dust and acetic anhydride, giving an amorphous powder, m. p. (very indefinite)

190°, the analyses of which give results agreeing approximately with those required for 1:1'-*diacetyltetrahydroquinokyl*. H. W.

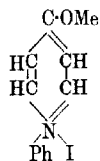
Fission of γ -Pyrone by Aniline and N-Phenyl-4-pyridone.

W. BORSCHÉ and IRIS BONACKER (*Ber.*, 1921, 54, [B], 2678—2686).— γ -Pyrone is readily converted by aniline into di-anilino-vinyl ketone, $\text{CO}(\text{CH}:\text{CH}\cdot\text{NPh})_2$, which easily loses aniline and passes into 1-phenyl-4-pyridone. The latter may be regarded, not only as a γ -pyridone derivative, but also as an *N*-disubstituted aromatic amine of the type of dimethylaniline. It exhibits, however, few of the reactions typical of this type of substance. Its indifference towards ketonic reagents, alkyl haloids, and nitrous acid has led Smernov (*A.*, 1921, i, 594) to regard it as an internal ammonium oxide (annexed formula). This view is not shared by the authors, since the quinquevalency of the nitrogen atom is opposed to its ability to add Grignard's reagents. They consider



that its stability is due to the unsaturated nature of the two carbon atoms attached to the nitrogen atom and the consequent greater demand on its valency whereby its power of influencing reactions in the aromatic portion of the molecule is correspondingly diminished. If this is the case, 1-phenyl-4-piperidone should exhibit the reactivity of an *N*-dialkylaniline. Since the ketone could not be prepared in sufficient quantity, this point has not been tested experimentally, but it is shown that the corresponding saturated secondary alcohol is a highly reactive substance.

Bishydroxymethylencetonedianilide [*di-anilino-vinyl ketone*], yellow, silky needles, m. p. 150°, is prepared by the action of aniline on γ -pyrone in dilute acetic acid solution at the atmospheric temperature (a substance, $\text{C}_{17}\text{H}_{16}\text{ON}_2$, m. p. 167°, is obtained as by-product in quantity too small for extended investigation). Fission of the γ -pyrone ring can also be effected by substituted anilines and its homologues if the latter possess pronounced basic properties; the corresponding *p-toluidino*-, pale yellow leaflets, m. p. 167°, and *m-nitranilino*-compounds, m. p. 223°, are described in detail. (*xx*-Dimethyl- γ -pyrone, on the other hand, appears to be stable towards aniline.) The dianilino-ketone is converted by hydrochloric acid, by sodium ethoxide, or by distillation in a vacuum into 1-phenyl-4-pyridone, long, colourless needles, m. p. (+2H₂O) 104—105°. Anhydrous 1-phenyl-4-pyridone, m. p. 116° (Smernov, *loc. cit.*, gives 125°), is conveniently prepared by distillation of aniline chelidonate under diminished pressure.



The corresponding *picrate*, yellow leaflets, m. p. 190°, and *methiodide*, colourless rhombohedra, m. p. 146°, are described; the latter, however, appears to be a *pseudomethiodide* (annexed formula), since the corresponding hydroxide passes into 1-phenyl-4-pyridone and methyl alcohol when its aqueous solution is evaporated. 1-Phenyl-4-pyridone forms an additive compound with magnesium methyl iodide, from which the parent substance is regenerated by dilute acid.

4-Hydroxy-1-phenylpiperidine, m. p. 69–70°, is prepared by the reduction of 1-phenyl-4-pyridone by sodium in boiling alcoholic solution. The *picrate*, dark yellow needles, m. p. 145–147°, *methiodide*, m. p. 153–155°, *benzoate*, coarse, colourless prisms, m. p. 102–103°, and *p-nitrobenzoate*, yellow leaflets, m. p. 156°, are described. 4-Hydroxy-1-phenylpiperidine does not react simply with nitrous acid, since the secondary alcoholic group is liable to be attacked, but the formation of a *p-nitroso-derivative* is established by the isolation of the corresponding gallocyanin dye, $C_{25}H_{31}O_7N_2Cl$, bluish-green needles, m. p. 140°. With a diazotised solution of aniline, 4-hydroxy-1-phenylpiperidine gives *4-hydroxy-1-p-benzenazo-phenylpiperidine*, small, brown crystals, m. p. 127° (*benzoyl derivative*, m. p. 125°), whilst with diazotised sulphanilic acid it gives the corresponding *sodium salt*, $C_{17}H_{16}O_4N_3SNa \cdot 2H_2O$, which is reduced by stannous chloride and hydrochloric acid to *4-hydroxy-1-p-aminophenylpiperidine*, colourless leaflets, m. p. 158° (*dibenzoyl compound*, colourless leaflets, m. p. 195°). *Di-4-hydroxypiperidino-4-phenylmethane*, $CH_2(C_6H_4 \cdot C_2NH_3 \cdot OH)_2$, colourless leaflets, m. p. 162°, is prepared from the base by the action of formaldehyde and hydrochloric acid.

The oxidation of 4-hydroxy-1-phenylpiperidine to 1-phenyl-4-piperidone has not been effected in a satisfactory manner; the latter substance has been prepared in small quantity by hydrogenation of 1-phenyl-4-pyridone by Skita's method and is identified as the compound, $NPh \langle \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} \rangle C:N:NH \cdot CO \cdot NPh$, yellow leaflets, m. p. 199° (decomp.).

H. W.

Benzyl Ester of 2-Phenylquinoline-4-carboxylic Acid.

A. GAMS and O. KAISER (U.S. Pat., 1378343).—Benzyl 2-phenylquinoline-4-carboxylate is prepared as follows: Sodium 2-phenylquinoline-4-carboxylate is heated in acetone and treated with benzyl chloride, gradually added, the acetone is distilled off, the residue is mixed with water and extracted with ether or benzene. The solution in the volatile solvent thus obtained is washed with sodium carbonate and with water and dried with calcium chloride and then treated with dry gaseous hydrogen chloride. The hydrochloride of the benzyl ester thus formed is a fine, crystalline, yellow powder. It is dissolved in alcohol, decomposed by adding solid sodium carbonate, and separated by filtration from the sodium chloride. By concentrating the solution the ester crystallises. It may be purified by recrystallisation from alcohol or ether. It has m. p. 77–78° and is citron-yellow. (CHEMICAL ABSTRACTS.)

Certain Derivatives of Arylated Cinchonic Acids. KARL W. ROSENMUND (*Ber.*, 1921, **54**, [B], 2893–2896).— α -Phenylcinchonic acid (2-phenylquinoline-4-carboxylic acid) is extensively used in pharmacy under the name "Atophan." In this connexion its allyl ester is particularly useful by reason of its low melting point, solubility in fat, and ready absorption by the skin. A number of unsaturated esters of differently substituted cinchonic acids are described, which, however, do not possess these properties.

2-Phenylquinoline-4-carboxylic acid is converted by boiling thionyl chloride into 2-phenylquinoline-4-carboxyl chloride, m. p. 81—82°. *Allyl* α -phenylcinchonate is a pale yellow liquid, b. p. 265°/15 mm., 215°/0.8 mm., m. p. 30°. The corresponding *cinnamyl* ester has m. p. 83°. *Allyl* 2-phenyl-6-methylquinoline-4-carboxylate forms pale yellow needles, m. p. 75—76°. *Allyl* 2-piperonylquinoline-4-carboxylate, m. p. 61°, β -*dibromo-n-propyl* 2-phenylquinoline-4-carboxylate, m. p. 75°, β -*dibromo- α -phenyl-n-propyl* 2-phenylquinoline-4-carboxylate, needles, m. p. 103°, and β -*dibromopropyl* 2-piperonylquinoline-4-carboxylate, m. p. 102—103°, are also described. H. W.

Isomerism of the isoOxazolecaboxylic Acids. VI. M. BETTI and S. BERLINGOZZI (*Gazzetta*, 1921, 51, ii, 229—238).—It has been shown (Betti and Alessandrini, A., 1915, i, 713; Betti, A., 1915, i, 896; Betti and Berlingozzi, A., 1915, i, 996, 997; Betti and Pacini, A., 1916, i, 222) that two 3:5-diphenylisooxazole-4-carboxylic acids, m. p. 153° and 233° respectively, and two 5-phenyl-3-methylisooxazole-4-carboxylic acids, m. p. 157° and 189° respectively, may be obtained. It is now found that, in either case, the acid with the lower melting point represents the unstable form and may be converted by boiling concentrated alkali hydroxide solution into the less readily fusible, stable isomeride; the inverse change has not been found possible.

These results explain (1) why the amide obtained from 3-phenyl (or methyl)-4-benzylidencisooxazolone may yield the one acid when treated with dilute alkali hydroxide solution and the other when treated with the concentrated alkali, it being the amide of the unstable acid, and (2) why the ethyl ester obtained by the action of hydroxylamine on ethyl benzoyl- (or acetyl)-acetoacetate is hydrolysable only to the stable isomeric acid, with which it corresponds. The amides of the stable acids, and the ethyl esters of the unstable acids, have now been prepared.

The isomerism of these acids may be due to the presence in the one form of a double ring, thus $\text{O} \begin{array}{c} \diagup \text{C} \text{Ph} \cdot \text{C} \cdot \text{CO}_2\text{H} \\ \diagdown \text{N} \text{—} \text{CR} \end{array}$; as this formula

contains an asymmetric carbon atom, experiments are being made on the optical resolution by means of alkaloids.

The stable form of 3:5-diphenylisooxazole-4-carboxylic acid, m. p. 233°, gives the following derivatives: *chloride*, which was obtained slightly impure in long, silky, almost white needles, m. p. 88—89°. *Amide*, $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_2$, which forms opaque, white, spherical, crystalline aggregates, m. p. 223°. *Anilide*, $\text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_2$, crystallising in groups of small, yellow needles, m. p. 188°. The isomeric unstable acid, m. p. 153°, gives an *anilide*, crystallising in lustrous, deep yellow leaflets, m. p. 236°; the *ethyl* ester, obtained as an orange-yellow oil, and the *chloride*, obtained as a viscous, orange-yellow substance, could not be purified.

The stable form of 5-phenyl-3-methylisooxazole-4-carboxylic acid, m. p. 189°, yields: a dense, oily, yellow *chloride*, difficult to purify; an *amide*, $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_2$, crystallising in opaque, white,

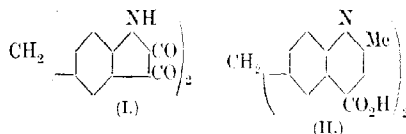
mammillary aggregates, m. p. 205°; and an *anilide*, which crystallises in groups of silky, white needles, m. p. 160°. The isomeric unstable modification, m. p. 157°, forms an oily, uncrystallisable *chloride*; an *anilide*, separating in lustrous, brown crystals, m. p. 179°, and an *ethyl ester*, which was obtained as a dense, intractable oil. T. H. P.

2:4-Diketo-5-phenyl-5-ethyltetrahydro-oxazole. J. ALTWEGG and D. EBIN (U.S. Pat., 1375949).—2:4-Diketo-5-phenyl-5-ethyltetrahydro-oxazole is prepared by dissolving 450 grams of α -phenyl- β -methyl-lactamide in 3 litres of boiling toluene, adding 700 grams of anhydrous potassium carbonate with stirring, slowly adding 300 grams of ethyl chloroformate, heating the mixture for an hour, adding cold water, decanting, and treating the liquid with sulphuric acid. An oily substance separates, which after some time solidifies to a crystalline mass, from which crystals, m. p. 63°, b. p. 176°/3 mm., are obtained after cooling. The aqueous solution has an acid reaction and forms salts with alkali or alkaline-earth metals and magnesium. The 5-methyl derivative, m. p. 70°, may be similarly produced from α -phenyl-lactamide.

CHEMICAL ABSTRACTS.

A New Synthesis of Oxazines. ARTHUR FAIRBOURNE and HAROLD TOMS (T., 1921, **119**, 2076—2078).

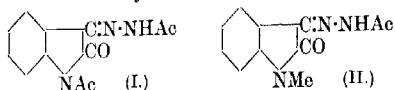
Isatin and its Derivatives. III. 5:5'-Di-isatylmethane and its Conversion into Quinoline Derivatives. W. BORSCHÉ and R. MEYER (Ber., 1921, **54**, [B], 2841—2843; cf. Borsche and SANDER, A., 1915, i, 299).—*p*-Diaminodiphenylmethane is readily converted by Sandmeyer's method (A., 1919, i, 318) through 4:4'-di(oximinooacetyl-amino)-diphenylmethane, yellow plates, m. p. 212°, into 5:5'-di-isatylmethane (I), a reddish-yellow powder which does not melt at 300°.



The latter compound readily combines with ketones, thus with acetone it yields 6:6'-methylene-di-(2-methylquinoline-4-carboxylic acid) (II), a yellow powder, m. p. above 320°, and this when distilled with lime, is converted into 6-diquinolylmethane, colourless plates, m. p. 142°, which forms a yellow *picrate*, darkens at 215°, m. p. 234° (decomp.). With acetophenone 5:5'-di-isatylmethane forms 6:6'-methylene-di-(2-phenylquinoline-4-carboxylic acid), m. p. 265° (decomp.), which when distilled with lime yields diquinolylmethane, silvery, glistening plates, m. p. 205°. F. M. R.

Isatin and its Derivatives. IV. The Action of Hydrazine on Isatin and 1-Methylisatin. W. BORSCHÉ and ROBERT MEYER (Ber., 1921, **54**, [B], 2844—2853).—The interaction of hydrazine

and isatin should result, according to the conditions, in the formation of isatin hydrazone or di-isatinazine, but Curtius and Thun (A., 1891, 1360) obtained only the former, and regarded it as a hydrazo-compound ($\text{C} \begin{smallmatrix} \text{NH} \\ \diagup \\ \text{NH} \end{smallmatrix}$). Staudinger and Kupfer (A., 1911, i, 751), on the other hand, concluded that the reaction products of hydrazine with aldehydes or ketones are hydrazones, and this view is supported by the investigation of the action of hydrazine on isatin and 1-methylisatin. If the products are hydrazo-compounds, the derivative of isatin should yield a triacetyl compound and the derivative of 1-methylisatin a diacetyl compound. Actually they yield diacetyl (I) and monoacetyl (II) compounds respectively, identical with the condensation products of acetylhydrazine with 1-acetylisatin and 1-methylisatin:



Isatinhydrazone can be condensed with isatin or aldehydes under suitable conditions, the reaction being facilitated in most cases by the presence of a trace of mineral acid, but condensation does not occur with ketones.

Isatinhydrazone, small, flat, yellow needles, m. p. 237—238° (Curtius and Thun gave 229°), sublimes without decomposition in a vacuum, dissolves in hot dilute sodium hydroxide with an orange-red colour, and on cooling slender, dark yellow needles (*o*-aminophenylglyoxylic acid-hydrazone sodium salt?) separate, from which isatinhydrazone is regenerated by acetic acid. 1-Acetyl-isatin-acetylhydrazone, yellow needles, m. p. 178°, is obtained by the action of acetic anhydride on isatinhydrazone, or by the action of acetylhydrazine on 1-acetylisatin in alcoholic solution. Benzylideneisatinazine, orange-red needles, m. p. 195° (decomp.), is obtained by the interaction of isatinhydrazone and benzaldehyde in alcoholic solution.

Piperonylideneisatinazine, small, orange-red needles, m. p. 250—251° (decomp.), is obtained by the interaction of isatinhydrazone and piperonaldehyde in alcoholic solution in presence of a drop of fuming hydrochloric acid.

p-Nitrobenzylideneisatinazine forms orange-red plates, m. p. 250—251° (decomp.). Di-isatinazine, glistening, dark red needles, decomposing at 295—296°, is best prepared by boiling an alcoholic solution of isatinhydrazone with isatin in presence of a few drops of fuming hydrochloric acid; it is hydrolysed by acetic acid and fuming hydrochloric acid to isatin and hydrazine, and with acetic anhydride it forms only a monoacetyl derivative, dark yellow, flat needles, decomposing at 220°. In continuation of a former investigation (A., 1902, i, 186), an attempt was made to convert Marchlewski's semicarbazone of isatin (A., 1896, i, 449) into the azine by boiling with aniline. The product was, however, the phenyl-carbamylhydrazone, $\text{C}_6\text{H}_5\text{ON} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NHPh}$, yellow needles,

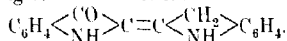
m. p. 233° (decomp.). 1-Methylisatinhydrazone forms small, yellow, glistening needles, m. p. $107-108^{\circ}$, is soluble in most organic solvents, but insoluble in dilute sodium hydroxide; it forms a red picrate, m. p. 112° , and a red hydrochloride, m. p. 182° . 1-Methylisatinacetylhydrazone crystallises in thin, yellow needles, m. p. 143° . Benzylidene-1-methylisatinazine forms red plates, m. p. 156° . p-Nitrobenzylidene-1-methylisatinazine forms small orange-yellow needles, m. p. $245-246^{\circ}$. Di-1-methylisatinazine crystallises in light red needles, decomposing at $240-245^{\circ}$ after darkening at about 235° .

There is a great similarity between the behaviour of isatin and that of 1-methylisatin with hydrazine, but the corresponding isatic acids (o-aminophenylglyoxylic acids) in acetic acid solution exhibit a remarkable difference in their behaviour when treated with hydrazine. o-Aminophenylglyoxylic acid yields an intermediate product, $C_{16}H_{14}O_4N_4 \cdot 2H_2O$, a pale yellow, crystalline powder, which is instantaneously converted into di-isatinazine by alcohol containing some hydrochloric acid. 1-o-Methylaminophenylglyoxylic acid, on the other hand, under similar conditions, yields a second hydrazone, oblique-angled, red prisms, m. p. $162-163^{\circ}$, believed to be a stereoisomeride of that already described. F. M. R.

Octabromindigotin. EUG. GRANDMOUGIN (*Compt. rend.*, 1921, **173**, 982-985).—Tetrabromoanthranilic acid, by the action of formaldehyde, gives a formalide, $C_8H_3O_2NBr_4$, which yields a nitrile and the latter on hydrolysis yields the glycine of tetrabromoanthranilic acid. The glycine when boiled with acetic anhydride gives acetyltetrabromindoxyllic acid, which in ammoniacal solution is readily saponified and oxidised, giving octabromindigotin. On oxidation in acetic acid solution with chromic acid, octabromindigotin gives tetrabromoisatin, and on reduction a leuco-derivative, the yellow sodium salt of which is only sparingly soluble. The original indigotin has a redder colour than the hexabromindigotin.

W. G.

Deoxyindigotin. W. BORSCHKE and ROBERT MEYER (*Ber.*, 1921, **54**, [B], 2854-2856).—An alcoholic suspension of indigotin is unaffected by boiling with hydrazine, but on adding sodium hydroxide and boiling for several hours, a deep green solution is obtained which deposits a yellow, crystalline precipitate on oxidation by air. This product, $C_{16}H_{12}ON_2$, crystallises from 200 times its weight of glacial acetic acid in small, greenish-yellow needles, m. p. 317° . The authors name the product *deoxyindigotin*, and ascribe the following constitution to it:



Neither deoxyindigotin nor the solution from which it is obtained are suitable for dyeing, but when deoxyindigotin is sulphonated with 36 times its weight of sulphuric acid for three-quarters of an hour at $40-45^{\circ}$ it yields a monosulphonic acid, the sodium salt of which dyes wool or silk in golden-yellow shades which are very

fugitive to light. Similar deoxy-compounds are obtained by the action of hydrazine and sodium hydroxide on 5:5'- or 7:7'-dimethylindigotin, or dibromoindigotin, but thioindigo red is only converted into its leuco-compound.

F. M. R.

Benzoylation and Benzoylation of 2:5-Diketopiperazine. TAKAOKI SASAKI and TOKUDJI HASHIMOTO (*Ber.*, 1921, **54**, [B], 2688—2693).—2:5-Diketo-1:4-dibenzoylpiperazine is prepared by the gradual addition of benzoyl chloride to a suspension of glycine anhydride in pyridine and subsequent heating of the mixture on a water-bath; it forms colourless crystals, m. p. 239—240°, whereas Scheiber and Reckleben (*A.*, 1913, i, 969) record m. p. 116°. It is smoothly converted into hippuric acid by means of sodium hydroxide solution at 37°, 2:5-Diketo-1:4-dibenzoylpiperazine (cf. Mason and Winder, T., 1894, **65**, 190; Mannich and Kuptal, *A.*, 1912, i, 217) cannot be prepared by the action of sodium ethoxide and benzyl chloride on glycine anhydride but is readily formed from diacetylglycine anhydride under similar conditions; it has m. p. 173—174°. The stability of the ring system is remarkably increased by the introduction of the two benzyl groups.

H. W.

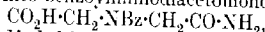
Diketopiperazines. XI. 3:5-Diketo-1-benzylhexahydro-1:4-diazine. J. V. DURSKEY and E. DINGEMANSE (*Ber.*, 1921, **54**, [B], 2659—2667; cf. *A.*, 1919, i, 289).—Iminodiacetonitrile, $\text{NH}(\text{CH}_2\text{CN})_2$, m. p. 78°, is conveniently prepared by the action of aqueous hydrocyanic acid (10%) on hexamethylenetetramine and is benzylated by the gradual addition of the nitrile and pyridine to benzyl chloride, which is heated at the temperature of boiling water. *Benzyliminodiacetonitrile*, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CH}_2\text{CN})_2$, large, prismatic crystals, m. p. 45—45.5° (the unstable *hydrochloride*, m. p. 105°, is described), is hydrolysed by boiling aqueous barium hydroxide solution to *benzyliminodiacetic acid*, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$, colourless, matted needles, m. p. 197—198° (decomp.). The substance behaves definitely as a monobasic acid and yields only a *monopotassium* salt even when treated with two molecular proportions of potassium hydroxide. The colourless *zinc* salt, $\text{C}_{11}\text{H}_{11}\text{O}_4\text{NZn}$, and the pale blue *copper* salt, $\text{C}_{11}\text{H}_{11}\text{O}_4\text{NCu}$, are described. The latter gives an azure blue additive *product*. $\text{C}_{11}\text{H}_{11}\text{O}_4\text{NCu}\cdot\text{NH}_3\cdot 2\text{H}_2\text{O}$, with ammonia. *Benzyliminodiacetic acid* gives a *nitrate*, $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}\cdot\text{HNO}_3$, colourless needles, m. p. 117° (decomp.), and a *hydrochloride*, $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}\cdot\text{HCl}$, decomp. 197°. *Benzyliminodiacetonitrile* is transformed by methyl-alcoholic hydrogen chloride into *methyl benzyliminodiacetate hydrochloride*, m. p. 210°, which, however, could not be isolated in the homogeneous condition. The corresponding *dimethyl* ester could only be obtained as a pale yellow, viscous liquid which decomposes when distilled under diminished pressure. The corresponding *diethyl* ester is a brownish-yellow, viscous liquid with similar properties; in the form of its hydrochloride, the latter is converted by ammonia into its *ethyl hydrogen* ester and, finally, into the *diamide*, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CH}_2\text{CO}\cdot\text{NH}_2)_2$.

pale yellow, glistening needles, m. p. (anhydrous) 166° ($+1\text{H}_2\text{O}$), m. p. 159° , which can also be prepared by the action of hydrogen peroxide on the nitrile. The anhydrous *hydrochloride* and its *monohydrate*, m. p. 222° (decomp.), are described. When heated at $180\text{--}190^{\circ}$ under 8 mm. pressure, the diamide is transformed into *benzyliminodiacetamide* [*3:5-diketo-1-benzyl-1:4-hexahydrodiazine*], $\text{CH}_2\text{Ph}\cdot\text{N}\langle\text{CH}_2\cdot\text{CO}\rangle\text{NH}$, yellowish-white crystals, m. p. 106° .

H. W.

Diketopiperazines. XII. Attempted Preparation of 1-Benzoyl-3:5-diketo-hexahydro-1:4-diazine. J. V. DUBSKY and E. HOHER (*Ber.*, 1921, **54**, [B], 2667—2673; cf. preceding abstract).—A record of unsuccessful attempts to prepare 3:5-diketo-1-benzoylhexahydro-1:4-diazine from benzyliminodiacetamide by elimination of ammonia or from the corresponding monoamide by loss of water.

Benzyliminodiacetonitrile, colourless, lustrous leaflets, m. p. $131\text{--}133^{\circ}$ (cf. Bailey and Snyder, A., 1915, i, 389), is prepared conveniently by heating iminodiacetonitrile with a solution of benzoyl chloride in benzene at $110\text{--}120^{\circ}$; it is formed in small amount by the benzoylation of the iminodinitrile according to the Schotten-Baumann method. It could not be hydrolysed with hydrogen peroxide; it is converted by barium or potassium hydroxide almost exclusively into benzyliminodiacetomonoamide,



m. p. $190\text{--}191^{\circ}$. *Methyl benzyliminodiacetate*, $\text{NBz}(\text{CH}_2\cdot\text{CO}_2\text{Me})_2$, transparent prisms, m. p. $73\text{--}76^{\circ}$, is prepared by the action of benzoyl chloride on methyl iminodiacetate or, preferably, from the hydrochloride of the ester, benzoyl chloride, and sodium hydrogen carbonate. It is hydrolysed by aqueous barium hydroxide solution at the atmospheric temperature to *benzyliminodiacetic acid*, $\text{NBz}(\text{CH}_2\cdot\text{CO}_2\text{H})_2\cdot\text{H}_2\text{O}$, glassy prisms, m. p. $88\text{--}90^{\circ}$; the *barium* salt, colourless leaflets ($+1.5\text{H}_2\text{O}$), and the *copper* salt, pale blue powder ($+ \text{H}_2\text{O}$), are described. Benzyliminodiacetodiamide, $\text{NBz}(\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$, m. p. $225\text{--}227^{\circ}$, is obtained by the action of ammonia on a solution of the methyl ester in alcohol. H. W.

Diketopiperazines. XIII. J. V. DUBSKY, E. HOHER, and E. DINGEMANSE (*Ber.*, 1921, **54**, [B], 2674—2678; cf. preceding abstracts).—2:5-Diketopiperazine-1:4-diacetodi- α -naphthalide, $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{N}\langle\text{CO}\cdot\text{CH}_2\rangle\text{N}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, decomposing above 313° , is obtained by the action of methyl iminodiacetate hydrochloride on α -naphthylamine at $170\text{--}175^{\circ}$. In spite of manifold variations in the experimental conditions, it was not found possible to conduct the operation in such a manner as to lead to the production of the ketopiperazine, $\text{NH}\langle\text{CH}_2\cdot\text{CO}\rangle\text{N}\cdot\text{C}_{10}\text{H}_7$.

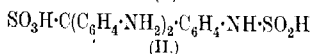
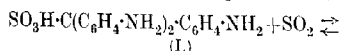
The preparation of phenyliminodiacetamide from aniline and chloroacetamide has been recorded previously (Dubsky and

Gränacher, A., 1918, i, 188); attempts to prepare the corresponding 2:6-dimethyl derivative by the use of α -chloropropionamide yielded a mixture of α -anilinopropionamide, $\text{NHPh}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}_2$, colourless, lustrous leaflets, m. p. 141° , and α -anilinopropionanilide, slender, silky needles, m. p. $126\cdot5^\circ$.

Hexaethylidenetetramine is highly resistant towards hydrocyanic acid. H. W.

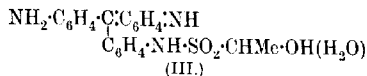
Rosaniline-sulphurous Acid and its Colour Reactions with Aldehydes. HEINRICH WIELAND and GEORG SCHEUING (*Ber.*, 1921, 54, [B], 2527—2555).—The hydrochloride of pararosaniline-leucosulphonic acid prepared by Hantzsch and Osswald (A., 1900, i, 256) was regarded as the substance which produces the well-known colour reactions with aldehydes. Subsequently, Dürsch-nabel and Weil (A., 1905, i, 947) obtained the free sulphonic acid, and products described as "neutral and acid sulphites" of pararosaniline. The latter authors' product is the free base of the former authors' hydrochloride, and is actually a trihydrate of pararosanilineleucosulphonic acid, crystallising in needles, whilst the so-called "acid sulphite" is the monohydrate of pararosanilineleucosulphonic acid, crystallising in oblique-angled plates. This sulphonic acid possesses an amphoteric character, and its hydrochloride has been described by Hantzsch and Osswald (*loc. cit.*). It forms a sodium salt, plates ($2\text{H}_2\text{O}$), and an ammonium salt, fine needles ($2\text{H}_2\text{O}$). Similar products are obtained from other dyes, namely, *Döbner's-violet-leucosulphonic acid*, small, quadrangular monoclinic, yellow crystals (H_2O), and *Crystal-violet-leucosulphonic acid*, faintly violet powder ($3\text{H}_2\text{O}$), which is extremely unstable.

The so-called "neutral sulphite" is the pararosaniline salt of pararosanilineleucosulphonic acid, metallic glistening crystals, $\text{C}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_3\cdot\text{SO}_3\cdot\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$. Similar colour salts of a mixed type have also been prepared, namely, the *Crystal-violet salt of pararosanilineleucosulphonic acid*, black, crystalline powder with a green, metallic lustre, and the *pararosaniline salt of Malachite-green-leucosulphonic acid*, black, microcrystalline powder with a green lustre. Pararosanilineleucosulphonic acid is not the substance which gives rise to colour reactions with aldehydes, for no reddish-violet colour is produced when acetaldehyde is added to a very dilute hydrochloric acid solution of pararosanilineleucosulphonic acid, and the latter can be isolated unaltered from the solution after removing the acetaldehyde in a vacuum. The colour reaction only occurs when the solution contains sulphurous acid. The solution of pararosanilineleucosulphonic acid (I) in sulphurous acid is regarded as containing the *N*-sulphinic acid (II), thus:

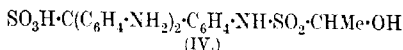


The sulphur dioxide attached to the amino-group in II can be

removed completely by iodine, which distinguishes it sharply from the sulphonic group attached to the carbon atom. The first stage in the reaction is the formation of the *N*-sulphinic acid, and the sulphonic group is introduced subsequently. When an aldehyde is added to the colourless dilute solution of the rosaniline-sulphurous acid an intense bluish-red colour is produced owing to the conversion of the benzenoid triphenylmethane derivative into a quinonoid compound by some hitherto unknown means. It was not known definitely whether the aldehyde colouring matter still contains sulphurous acid in some form, or whether it is identical with the reaction product obtained by the interaction of rosaniline and one or two molecular proportions of aldehyde. Actually the aldehyde colouring matter contains SO_2 . When a solution of pararosaniline reacts with one molecular proportion of sulphur dioxide and one molecular proportion of acetaldehyde, an insoluble colouring matter (III) separates in bluish-red flocks after a short time :



With an excess of sulphurous acid, a colourless, crystalline product ($4\text{H}_2\text{O}$) is formed :



This *N*-aldehyde-sulphurous acid pararosanilineleucosulphonic acid (IV) is also formed by the addition of acetaldehyde to a concentrated solution of pararosanilineleucosulphonic acid in a slight excess of aqueous sulphurous acid.

The colouring matter (III) is insoluble, whereas the colouring matter produced in the ordinary colour reaction with aldehydes is readily soluble, and is only formed when a further molecular proportion of sulphur dioxide is used, and the quantity of aldehyde is also increased. It would appear, therefore, that the latter colouring matter, when acetaldehyde is used, has the constitution : $\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{SO}\cdot\text{O}\cdot\text{CHMe}\cdot\text{OH})_2$. The instability of this colouring matter on keeping is due to the hydrolysis of the aldehyde-sulphurous complex as such, for that does not give rise to colour reactions.

F. M. R.

Trypaflavin [3:6-Diamino-1-methylacridinium Chloride].
 HANS THIEME (*Ber. deut. Pharm. Ges.*, 1921, **31**, 323—344).—Normal trypaflavin is composed of equimolecular quantities of two stereoisomeric forms, one of which on treatment of the sulphate in aqueous solution with barium hydroxide is converted into the true stable quaternary ammonium base, whilst the other breaks down into diaminoacridine with loss of methyl alcohol. The trypaflavin sulphate which is formed on adding sulphuric acid to the aqueous solution of the base after filtering off the diaminoacridine, no longer behaves as a dual substance when the treat-

ment with barium hydroxide is repeated, as no diaminoacridine is formed, but, instead, the theoretical quantity of the quaternary base. The different behaviour of the normal sulphate and the above salt was also demonstrated by conductivity measurements of the two salts in reaction with barium hydroxide. Whilst in the one case a very rapid fall in conductivity during the first few minutes was observed, in the latter case, where no diaminoacridine was formed, no such rapid fall in conductivity occurred. In each case there was a slow continuous decline, but this was due to absorption of carbon dioxide by the free base. G. F. M.

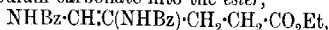
The Behaviour of certain Bisacylaminoethylene Derivatives prepared from Glyoxalines. A. WINDAUS, W. DÖRRIES, and H. JENSEN (*Ber.*, 1921, **54**, [B], 2745—2755).—A series of examples is given of the fission of the glyoxaline ring by isovaleryl chloride with the product of bisacylaminoethylenes, the catalytic hydrogenation of the latter to the ethane derivatives, and the conversion of these into the corresponding amines. The bisbenzoylaminoethylene compounds lose a molecule of benzoic acid and one of ammonia under the influence of alcoholic hydrogen chloride and pass into benzoylamino-ketones which are transformed by further action of the same reagent into aminoketones.

A well-cooled aqueous solution of glyoxaline is converted by alternate addition of small amounts of isovaleryl chloride and potassium hydroxide solution into *bisisovalerylaminoethylene*, which is conveniently characterised as its *dibromide*, slender needles, m. p. 164—165° (decomp.). Hydrogenation of the ethylene derivative in the presence of spongy palladium gives *bisisovalerylaminoethane*, $C_2H_4(NH \cdot CO \cdot C_4H_9)_2$, lustrous needles, m. p. 182°, which is converted by concentrated hydrochloric acid at 140° into ethylenediamine dihydrochloride. Bisbenzoylaminoethylene is transformed by boiling methyl alcoholic hydrogen chloride solution (10%) into aminoacetaldehyde, which is identified as glyoxalosazone.

4(5)-Methylglyoxaline is converted by isovaleryl chloride and reduction of the initial product into $\alpha\beta$ -*diisovalerylamino*propane, colourless, slender needles, m. p. 172—173°, which is transformed into $\alpha\beta$ -diaminopropane (*dipicrate*, yellow needles, m. p. 237° after previous darkening; dibenzoyl derivative, m. p. 192—193°). $\alpha\beta$ -Dibenzoylaminoethylene is transformed by alcoholic hydrogen chloride into aminoacetone.

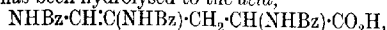
Hydrogenation of the product of the fission of histamine with isovaleryl chloride leads to the formation of $\alpha\beta$ -*triisovalerylamino*butane, slender needles, m. p. 196—197°, which is converted in the usual manner into $\alpha\beta$ -*triaminobutane trihydrochloride*, needles, m. p. 209—210° (corresponding *picrate*, small, yellow needles, decomp. about 225°). The fission of histamine with benzoyl chloride and sodium hydroxide has been described previously (Windaus and Vogt, A., 1907, i, 978); the product thus obtained is converted by alcoholic hydrogen chloride into $\alpha\delta$ -*dibenzoylamino- β -ketobutane*, $NHBz \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot NHBz$, small, colourless needles, m. p. 151° (*semicarbazone*, needles, m. p. 172—173°).

Ethyl glyoxaline-4-propionate oxalate is transformed by benzoyl chloride and sodium carbonate into the ester,



slender needles, m. p. 132—133° (the corresponding acid crystallises in needles, m. p. 156—157°); it is converted by boiling alcoholic hydrogen chloride into ethyl δ -benzoylamino- γ -ketovalerate, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, coarse prisms, m. p. 101° (semicarbazone, needles, m. p. 171°).

The fission of histidine methyl ester has been described by Kossel and Edlbacher (A., 1915, i, 285); the unsaturated ester thus produced has been hydrolysed to the acid,



small needles, m. p. 241°. The unsaturated ester is converted by hydrogen chloride dissolved in methyl alcohol into methyl α - δ -benzoylamino- γ -ketovalerate, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}(\text{NHBz})\cdot\text{CO}_2\text{Me}$, lustrous needles, m. p. 173—174°; it gives a phenylhydrazone, pale yellow leaflets, m. p. 221—222°.

H. W.

The Nitro- and Amino-derivatives of 4-Phenylglyoxaline.

REGINALD LINDSAY GRANT and FRANK LEE PYMAN (T., 1921, 119, 1893—1903).

Aziminobenzene (1:2:3-Benztriazole). G. CHARRIER and A. BERETTA (*Gazzetta*, 1921, 51, ii, 267—269).—Attempts were made to prepare *o*-benzoylamino-phenyldiazonium chloride by the action of nitrous acid on benzoyl-*o*-phenylenediamine, but it was found that, under the most varied conditions, this reaction yields

the benzoyl derivative of 1:2:3-benztriazole, $\text{C}_6\text{H}_4\langle\text{N}^{\text{Bz}}\rangle\text{N}$,

which crystallises in long, colourless needles, m. p. 112°. When dissolved in 95% alcohol and boiled in a reflux apparatus with 30% sulphuric acid for nine hours, this compound is hydrolysed to 1:2:3-benztriazole, which is conveniently prepared by this method.

T. H. P.

Preparation of Triazoles of the Aromatic Series (ψ -Azimides). KALLE & Co., AKT. GES. (D.R.-P., 338926; from *Chem. Zentr.*, 1921, iv, 709).—*o*-Aminoazo-dyes, in particular those which contain amino- and hydroxyl-groups in addition to the amino-group present in the ortho-position to the azo-group are treated with cuprammonium salts. The product from diazotised sulphanilic acid and *m*-tolylenediamine is dissolved in water and treated with ammonia. An aqueous solution of copper sulphate and 25% aqueous ammonia solution is added and the mixture is heated at 90° for a few hours. On cooling, the ammonium salt of 5-amino-2-*p*-sulphophenyl-6-methyl- ψ -aziminobenzene crystallises out.

5-Amino-2-phenyl- ψ -aziminobenzene, $\text{PhN}\langle\text{N}\rangle\text{C}_6\text{H}_3\cdot\text{NH}_2$, is simi-

larly obtained from benzeneazo-*m*-phenylenediamine. It crystallises from glacial acetic acid and has m. p. 183°. The dye from diazotised 5-aminosalicylic acid and *m*-tolylene diamine gives

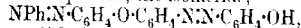
similarly 5-amino-2-*p*-hydroxy-*m*-carboxyphenyl-6-methyl- ψ -azimino-benzene, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{N}\langle\begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix}\rangle\text{C}_6\text{H}_2\text{Me}\cdot\text{NH}_2$. G. W. R.

Structure and Colour of the Azine Scarlets. JULIUS BEREND COHEN and HERBERT GRACE CRAIBTREE (T., 1921, 119, 2055—2070).

Ring Closure with Hydrazinedicarbonamides containing Sulphur. Dithiourazole and Iminothiourazole. EMIL FROMM (Ber., 1921, 54, [B], 2840).—The author has prepared previously many of the compounds described by Arndt and Milde in their recent publication (A., 1921, i, 813), and the account of the work will appear shortly in the *Annalen*. In general, the results obtained are in good harmony except in so far as the preparation of dithiourazole and iminothiourazole is concerned, for which the author prefers the older process. H. W.

The Electrochemical Oxidation of Azobenzene. FR. FICHTER and WOLFGANG JAECK (*Helv. Chim. Acta*, 1921, 4, 1000—1009).—Text-books of electrochemistry, in dealing with the question of the introduction of hydroxyl groups into the benzene nucleus by anodic oxidation, quote the conversion of azobenzene into tetrahydroxyazobenzene (Heilpern, A., 1898, i, 249) as a smooth reaction. Heilpern's analytical figures for the so-called tetra-acetyl derivative of tetrahydroxyazobenzene, however, represent a triacetyl derivative as regards the carbon content, although the hydrogen content does not agree with this. Repetition of the oxidation shows that the product resembles that obtained by Heilpern, and is formed by the hydroxylation of azobenzene, although it is not tetrahydroxyazobenzene, but a complex mixture. Two of the reaction products have been isolated in the form of their acetyl derivatives from this mixture by means of their different solubilities in benzene; *pp'*-diacetoxyazobenzene, readily soluble in benzene, m. p. 193.5°, which on hydrolysis yields *pp'*-dihydroxyazobenzene, brown crystals, m. p. 204°; *diphenyl-pp'*-bisazo-phenyl acetate, sparingly soluble in benzene, glistening orange-red crystals, m. p. 237°, which on hydrolysis yields *diphenyl-pp'*-bisazophenol, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, small, brown needles, m. p. 265°, the constitution was confirmed by synthesis from tetrazotised benzidine and phenol.

For purposes of comparison, the isomeride,



for which the name 4'-hydroxy-4:4'-bisazo-benzotyl ether is suggested, in which azobenzotyl represents the group $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4$, was synthesised; *p*-hydroxyazobenzene condensed with *p*-nitrochlorobenzene for twelve hours at 240° yields azobenzotyl-*p*-nitrophenyl ether, small, brown crystals, m. p. 125°, which is reduced in aqueous-alcoholic solution by sodium sulphide to azobenzotyl-*p*-aminophenyl ether, pale brown, glistening scales, m. p. 100—101°. Prolonged reduction converts the latter compound into its hydrazo-derivative, m. p. 212°, which is reoxidised by air to the azo-compound. When

azobenzoyl-*p*-aminophenyl ether is diazotised and coupled with phenol, 4'-hydroxy-4 : 4''-bisazobenzoyl ether, brown crystals, m. p. 198°, is formed; its acetyl derivative crystallises in plates, m. p. 183°.

F. M. R.

Action of Diazo-salts on Aromatic Sulphonamides. I. PAVITRA KUMAR DUTT, HUGH ROBINSON WHITEHEAD, and ARTHUR WORMALL (T., 1921, **119**, 2088—2094).

Separation of the Proteins of the Serum. M. PIETTRE and A. VILA (*Bull. Soc. Chim. Biol.*, 1921, **3**, 483—489).—A simplified method for the separation of serum-albumin and serum-globulin is described. Serum is neutralised with hydrochloric or sulphuric acid and the proteins are precipitated by addition of acetone or alcohol. Treatment of the precipitate with water removes the albumin, which is again precipitated, after filtration from the globulin, by addition of acetone.

E. S.

The Electric Charge of Hæmoglobin. L. MICHAELIS and Y. AIRILA (*Biochem. Z.*, 1921, **118**, 144—149).—Cataphoretic experiments show that hæmoglobin behaves as a complex ampholyte. At the isoelectric point, the cataphoretic movement is nil, and with increasing or decreasing P_H there is a continuous increase in the cataphoretic velocity. These results disprove Straub and Meier's contentions (A., 1921, i, 72).

H. K.

Viscosity of Gelatin Solutions. CLARKE E. DAVIS, EARLE T. OAKES, and HAROLD H. BROWNE (*J. Amer. Chem. Soc.*, 1921, **43**, 1526—1538).—Three kinds of gelatin have been examined to ascertain the effect on the viscosity of gelatin solutions of (a) the ageing of the solution, (b) the method of producing the solution, (c) the hydrogen-ion concentration, (d) the concentration of the gelatin, and (e) the hydrolysis of the solution. It is shown that viscosity determinations of gelatin solutions can be made by an Ostwald viscosimeter with a maximum error of 0.5%. Gelatin solutions increase in viscosity with age at different rates, depending on the concentration of the gelatin, the type of gelatin, and the hydrogen-ion concentration. For any given gelatin solution a maximum viscosity is attained at an age of solution of about twenty-four hours. A decrease in viscosity after the maximum is reached indicates bacterial decomposition. Gelatin solutions show a maximum viscosity at a hydrogen-ion concentration represented by $P_H=3.0-3.5$ at 25°. The viscosity of gelatin solutions is not a simple function of the concentration of the gelatin. Both the hydrogen and hydroxyl ions catalyse the hydrolysis of gelatin in solution, but the hydroxyl ion is more powerful in this respect than the hydrogen-ion. Excessive temperatures accelerate the hydrolysis of gelatin, whilst actual boiling of the solutions causes very rapid hydrolysis.

J. F. S.

An Unidentified Base among the Hydrolytic Products of Gelatin. DONALD D. VAN SLYKE and ALMA HILLER (*Proc. Nat. Acad. Sci.*, 1921, **7**, 185—186).—The non-amino-nitrogen precipitable from the products of the acid hydrolysis of proteins is

assumed to be entirely in the histidine and arginine. When arginine is estimated directly, the remaining non-amino-nitrogen is assumed to be histidine. A comparison of the histidine obtained on this assumption with that obtained by Koessler and Hanke's direct colorimetric method (A., 1920, ii, 67) gave satisfactory results for casein, cdestin, and fibrin, but not for gelatin. A hitherto unknown base must therefore be present among the products of the hydrolysis of gelatin which are precipitable by phosphotungstic acid. This was obtained by successive removal of the other bases from the phosphotungstate fraction, after removal of phosphotungstic acid. Attempts to crystallise the free base were unsuccessful. It is hygroscopic and decomposes slowly at 100°. The ratio of total nitrogen to amino-nitrogen is 2:1 and is not increased by prolonged boiling with 20% hydrochloric acid or by heating in a bomb tube with 25% sulphuric acid. It is concluded that it is not a peptide. G. W. R.

Origin of Melanin from Pyrrole. II. Action of Organ Extracts on Pyrrole. The Sepia of the Cuttlefish. PIETRO RONDONI (*Sperimentale*, 75, 33—44; from *Chem. Zentr.*, 1921, iii, 887).—An aqueous extract of the ink-sac of cuttlefish (previously freed from secretion) gives a distinct blackening with pyrrole. It is weaker in the case of an extract heated for ten minutes, but is deepened by addition of ferrous sulphate solution. Similar results are obtained with extract from the skin of frogs. The phenomenon is confined to melanogenic organs and is of colloidal character. A pyrrole oxydase may be present. The inky secretion (sepia) appears to be a suspensoid associated with a protective colloid which prevents precipitation by the electrolytes in sea-water. From the similar properties of sepia and Angeli's "pyrrole-black" it is concluded that a pyrrole ring occurs in the former. G. W. R.

Action of Hydrolytic Enzymes. II. MARC H. VAN LAER (*Bull. Soc. Chim. Belg.*, 1921, 30, 261—265; cf. A., 1921, ii, 445).—The author's hypothesis, that a hydrolytic enzyme owes its activity to its capacity for adsorbing substrate and hydrogen ions, involves the possibility of an enzyme acting on all hydrolysable substances which it adsorbs. In such a case, the optimal concentration of hydrogen ions should be independent of the particular substrate acted on, for this optimum is regarded as a characteristic of the enzyme itself, being the point beyond which the coagulating effect of further increases in the concentration of hydrogen ions, on the enzyme particles, preponderates over their catalytic effect on hydrolysis. Among the hydrolytic transformations effected by malt extract, those relating to starch, proteins, esters, and amygdalin (cf. A., 1921, i, 488) are all subject to the same optimal reaction, and may accordingly be due to one enzyme. J. H. L.

Some Errors in the Study of Invertase Action. WARREN C. VOSBURGH (*J. Amer. Chem. Soc.*, 1921, 43, 1693—1705; cf. Nelson and Vosburgh, A., 1917, ii, 252).—Invertase solutions are

subject to loss in activity when diluted, the magnitude of the loss varying with the invertase preparation and the substances present in the water used for the dilution. Dilution with distilled water results in less loss than is the case if very dilute acids are used and for practical purposes is consistent if the dilution is not too great. When an invertase solution is added to solutions containing sucrose, losses in activity are less than when the sucrose is absent. The velocity of hydrolysis of sucrose by invertase is greater when a citrate or acetate buffer is used as the source of hydrogen ions than when citric or acetic acid respectively is so used. Both dilute and stock solutions of invertase lose strength on keeping, the former faster than the latter. W. G.

Toxicity. I. The Action of Quinine on Invertase. PETER RONA and ERNST BLOCH (*Biochem. Z.*, 1921, **118**, 185—212).—The inhibitory action of quinine hydrochloride on invertase is dependent on the P_H of the solution. The more alkaline, the greater the toxic effect. This indicates that the free base is the active agent. The same applies to the action on paramœcia. Optochin, eucupin, and vuzin behave similarly, the two former being equivalent to quinine; vuzin is considerably more active. Quinidine has a greater toxic effect than quinine. H. K.

Toxicity. III. The Action of *m*- and *p*-Nitrophenols on Invertase. PETER RONA and EMERICH BACH (*Biochem. Z.*, 1921, **118**, 232—253).—The inhibitory action of these phenols is a time process. There is also a distinct threshold value for each, beyond which only a relatively small variation of concentration is possible without producing complete inhibition. The process is not reversible, this being attributed to an irreversible destruction of the ferment. H. K.

The Action of Metallic Copper and Silver on Diastase. The so-called Oligodynamic Phenomena. A. LUGER (*Biochem. Z.*, 1921, **117**, 153—160).—Diastase inactivated by contact with metals is more or less reactivated by treatment with certain salts such as potassium cyanide and sodium thiosulphate. H. K.

Enzymes. VIII. Conditions of Action of Amylases. W. BIEDERMANN and AMIN RUEHA (*Fermentforsch.*, 1921, **5**, 56—83; cf. A., 1921, **1**, 11, 468).—The results of previous investigators on the hydrogen- or hydroxyl-ion concentrations under which amylases act are fully discussed and their bearing on the different theories which have been advanced to explain enzyme action is considered.

As regards the retarding influence of hydroxyl ions on diastatic action, there exists always an upper limiting amount of enzyme for which the optimum activity persists in spite of the alkaline reaction. For less quantities of the enzyme, the action is retarded to an extent which increases as the amount of enzyme diminishes. Such "subliminal" amounts of enzyme may, however, be rendered active under the same reaction conditions if the degree of activity

and therewith the diastatic power is raised by addition of suitable ionic mixtures to the solution.

Similarly, the action of diastatic enzymes is prevented by a certain definite hydrogen-ion concentration, this depending, however, on the amount of enzyme present in the solution. Malt diastase is far more "acid-proof" than the ptyalin of saliva, the former exerting its optimum activity when the acidity is such that the action of the latter is prevented.

T. H. P.

Chemical Investigation of Amylases and Related Enzymes.

H. C. SHERMAN (*Carnegie Inst. Washington Yearbook*, 1919, 18, 328—330).—A neutral solution of sodium aspartate corrected the abnormally low results obtained by the action of purified pancreatic amylase on potato starch which had previously been purified by washing with very dilute alkali and subsequent thorough washing with specially purified water. The neutral solution of sodium aspartate also accelerated the rate of hydrolysis of wheat, maize, rice, and potato starches by purified pancreatic amylase, by purified malt amylase, by commercial pancreatin, or by saliva, but had no such action on their hydrolysis by a simple extract of malt, or by either the commercial or a laboratory preparation of the amylase of *Aspergillus oryzae*. When soluble starch was used as the substrate and the reducing sugar produced was estimated gravimetrically, similar results were obtained. When this technique was used, and asparagine was substituted for sodium aspartate, essentially similar results were obtained; however, the asparagine apparently produced a slight increase in the activity of taka-diastase. When both asparagine and a neutral solution of sodium aspartate were added to a digestion mixture, the results were such as were obtained by use of either of the two compounds in its optimum concentration. Thus the activating effects of aspartic acid and asparagine were interchangeable rather than additive; their effect was not due to a change in the hydrogen-ion concentration, or to the sodium ion, or to the mere concentration of electrolyte, since optimum concentrations of chlorides and phosphates were already present. The effect was, in a sense, specific, since neutral sodium aspartate increased the enzymic activity when the optimum amounts of chlorides and phosphates were present, but could not completely replace chlorides in the activation of pancreatic amylase. CHEMICAL ABSTRACTS.

Importance of Acidity for Cyanohydrin Synthesis and the Non-existence of Rosenthaler's *syn*-Emulsin. E. NORDEFELD (*Biochem. Z.*, 1921, 118, 15—33).—The formation of benzaldehyde-cyanohydrin is largely conditioned by the P_H of the solution, the synthetic action increasing rapidly with increase of P_H . The enzymatic nature of emulsin in this reaction is an unnecessary assumption, the increased velocity in its presence being due to removal of hydrogen-ions by adsorption of benzoic acid. The specificity of emulsin in producing optical activity in the hydroxy-nitrile formed is not necessarily enzymatic, as the results of Fajans (*A.*, 1908, ii, 268) with quinine and quinidine have shown. H. K.

Toxicity. II. The Action of Quinine on Serum-lipase.

PETER RONA and DORA REINICKE (*Biochem. Z.*, 1921, **118**, 213—231).—Quinine hydrochloride inhibits the action of lipase similarly to the inhibition produced by atoxyl (A., 1921, i, 69). The action depends on the P_H of the medium, being more pronounced with increasing P_H , and is independent of the particular salt of quinine used. The inhibiting action on animal sera is only obtained at concentrations of quinine one hundred to one thousand times that observed with human sera.

H. K.

The Enzyme Phosphatase-Phosphatase. H. P. BAREN-
PRECHT (*Biochem. Z.*, 1921, **118**, 254—255).—Euler and Ohlsen's experiments (A., 1912, i, 61) support the radiation hypothesis of enzyme action.

H. K.

Additive Reactions of, Phosphorus Haloids. II. The 1:4-Addition of Phosphenyl Chloride. JAMES B. CONANT and S. M. POLLACK (*J. Amer. Chem. Soc.*, 1921, **43**, 1665—1669; cf. A., 1920, i, 454).—Dichlorophenylphosphine reacts with phenyl styryl ketone in acetic acid solution to give *phenyl-β-benzoyl-α-phenylethylphosphinic acid*, $\text{COPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{PPhO}\cdot\text{OH}$, m. p. 220—225° (decomp.). In acetic anhydride as a solvent, the product is an unsaturated cyclic *anhydride*, $\text{CH}\begin{smallmatrix} \text{CHPh} \\ \text{CPh}\cdot\text{O} \end{smallmatrix} \text{PPhO}$, which

readily reacts with water to give the ketophosphonic acid. The structure of the anhydride is shown by the fact that it combines with one equivalent of bromine and the product reacts with water to give two stereoisomeric *phenyl-β-bromo-β-benzoyl-α-phenylethylphosphinic acids*, $\text{CHBzBr}\cdot\text{CHPh}\cdot\text{PPhO}\cdot\text{OH}$, which may also be prepared by bromination of the ketophosphonic acid. One has m. p. 150° and the other m. p. 195° (decomp.). They are both decomposed by aqueous alkali, giving phenyl styryl ketone, hydrogen bromide, and phenylphosphonic acid.

W. G.

Addition Reactions of Phosphorus Haloids. III. The Reaction with Distyryl Ketone and Phenyl Cinnamylidenemethyl Ketone.

JAMES B. CONANT, ALBERT H. BUMP, and HAROLD S. HOLT (*J. Amer. Chem. Soc.*, 1921, **43**, 1677—1684; cf. preceding abstract).—Phosphorus trichloride acts on distyryl ketone in acetic acid solution to give *β-cinnamoyl-α-phenylethylphosphonic acid* (cf. A., 1918, i, 74), which, when acted on by bromine in chloroform solution, yields *α-phenyl-β-(α'β'-dibromo-β'-phenylpropionyl)-ethylphosphinic acid*.

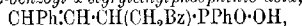
$\text{CHPhBr}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{PO}(\text{OH})_2$,
m. p. 180—182°. This compound readily loses hydrogen bromide under the influence of alcoholic potassium hydroxide, giving *α-phenyl-β-(α'-bromocinnamoyl)-ethylphosphinic acid*,

$\text{CHPh}\cdot\text{CBr}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{PO}_3\text{H}_2$,
m. p. 130—132°, which on oxidation with ozone gives hydrogen bromide, benzoic acid, and *α-phenyl-β-glyoxyethylphosphinic acid*, $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{PO}_3\text{H}_2$, m. p. 183° (decomp.), and this phosphonic acid on heating loses carbon monoxide, yielding *α-phenyl-β-carboxyethylphosphinic acid*.

d*

A similar series of reactions occurred when the phosphorus trichloride was replaced by phosphenyl chloride. The products obtained were *phenyl- α -phenyl- β -cinnamoyl-ethylphosphinic acid*, $\text{CHPh:CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{PPh}\cdot\text{O}\cdot\text{OH}$, m. p. 235–236°; *phenyl- α -phenyl- β -carboxyethylphosphinic acid*, m. p. 212°; *phenyl- α -phenyl- β -(α' , β' -dibromophenylpropionyl)-ethylphosphinic acid*, m. p. 195° (decomp.); *phenyl- α -phenyl- β -(α' -bromocinnamoyl)-ethylphosphinic acid*, m. p. 200°.

Phenyl cinnamylidenemethyl ketone condensed with phosphorus trichloride in acetic anhydride to give a poor yield of *β -benzoyl- α -styryl-ethylphosphinic acid*, $\text{CHPh:CH}\cdot\text{CH}(\text{CH}_2\text{Bz})\cdot\text{PO}_3\text{H}_2$, m. p. 159–161°, and with phosphenyl chloride in acetic acid solution to give *phenyl- β -benzoyl- α -styryl-ethylphosphinic acid*,



m. p. 200°, which on oxidation with ozone gave benzaldehyde as one of the products, the combination thus taking place in the 1:4-position.

W. G.

New Organic Compounds of Phosphorus. IV. Phosphineimines. H. STAUDINGER and ERNST HAUSER (*Helv. Chim. Acta*, 1921, 4, 861–886).—It has been shown previously (Staudinger and Meyer, A., 1920, i, 106) that phosphines react with azides to give phosphazides which decompose spontaneously into phosphineimines: $\text{NPh:N:N} + \text{PPh}_3 \rightarrow \text{NPh:N:N:PPh}_3 \rightarrow \text{NPh:PPh}_3$. By operating at a low temperature, it has now been found possible to effect the isolation of certain phosphazides. The behaviour of phosphines towards azides has been more fully examined.

The greatest reactivity towards phenyl- and benzoyl-azides is exhibited by tertiary phosphines, among which the alkyl compounds are the most active. Triphenylstibine, triphenylarsine, and a number of tertiary amines are found to be indifferent towards azides, and the substances thus conform to the general rule that phosphorus shows the most pronounced tendency to pass into the quinquivalent state. Triphenylphosphine and triethylphosphine react readily in cold dilute solution with a number of azides, and the reaction does not appear to be influenced to a marked degree by the presence of substituents in the latter. It therefore appears probable that the azides, the aliphatic diazo-compounds, and nitrous oxide, all of which behave in the same manner towards phosphines, are to be regarded as substances possessing the unsaturated group, N:N , for which the name "azen" is proposed. The independence of the reaction on the presence of substituents in the nitrogenous component thus receives an explanation, since it is unlikely that the behaviour of the terminal nitrogen atom would be influenced greatly by a change in group at the third nitrogen atom.

The reactivity of the phosphineimines depends greatly on the presence of substituents. In general, derivatives of triethylphosphine are more active than those of triphenylphosphine and *N*-alkylated phosphineimines react more readily than the corres-

pending *N*-arylated compounds. Benzoylated phosphineimines are relatively very stable. Generally, the phosphineimines are readily hydrolysed in accordance with the scheme $\text{NR:PR}_3 + \text{H}_2\text{O} \rightarrow [\text{R}_3\text{P}(\text{OH})\cdot\text{NHR}] \rightarrow \text{R}_3\text{P:O} + \text{NH}_2\text{R}$. They yield salts with acids, some of which are stable towards cold water. They react readily with carbonylene derivatives containing twin double bonds (carbon dioxide, carbimides, and ketens), giving oxides of the tertiary phosphines, and a similar change is observed with thio-carbonylene compounds and other substances with twin double bonds (sulphur dioxide, etc.). On the other hand, they do not react in the cold with substances containing a simple carbonyl group even if the latter is unusually activated. Similarly, simple reactions are not observed with other substances containing an unsaturated bond, such as nitrosobenzene.

Phosphine does react with an ethereal solution of phenylazide or benzoylazide. Phenylphosphine and phenylazide evolve nitrogen violently after some time, but the other products have not been examined.

The following substances are described. *Triphenylphosphineimine azide*, $\text{PPh}_3\cdot\text{NH}_3\text{N}_3\text{H}$ (from triphenylphosphine and hydrogen azide in benzene solution), a colourless, crystalline powder, m. p. 196° (decomp.), which is stable in dilute aqueous solution, but is hydrolysed by dilute acids to triphenylphosphine oxide. *Triphenylphosphinemethylimine*, NMe:PPh_3 , a colourless, crystalline mass which is very sensitive towards moisture, m. p. (about) $62-65^\circ$; it is converted by carbon dioxide into triphenylphosphine oxide and methylcarbimide and by carbon disulphide into triphenylphosphine sulphide and methylthiocarbimide. *Ethylazide*, a colourless, mobile liquid, b. p. 45° . *Triphenylphosphine-ethylimine*, a colourless, crystalline substance, m. p. (indefinite) 90° , which is transformed by ethyl iodide into the compound, $\text{C}_{22}\text{H}_{25}\text{NPI}$, m. p. $164-165^\circ$. Ethyl azidoacetate and triphenylphosphine give a glassy mass which is hydrolysed to triphenylphosphine oxide and glycine ester hydrochloride and is transformed by methyl iodide into the compound, $\text{C}_{22}\text{H}_{25}\text{O}_2\text{NPI}$, m. p. $103-104^\circ$.

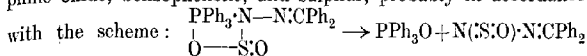
Triphenylphosphinephenylimine is transformed by phenylcarbimide into triphenylphosphine oxide and carbodiphenyldi-imide, and by benzophenone, after prolonged heating at 150° , into triphenylphosphine oxide and benzophenoneaniline. Benzaldehyde at 100° gives triphenylphosphine oxide and benzylideneaniline. Sulphur dioxide very readily gives thionylaniline, whereas a reaction is not observed with nitrobenzene, diphenyl-*N*-phenylnitron, iodo-benzene, or diphenylsulphoxide. *Triphenylphosphine- α -naphthylazide*, $\text{C}_{10}\text{H}_7\text{N:N:N:PPh}_3$, a yellow, crystalline powder, decomp. $63-65^\circ$. *Triphenylphosphine- α -naphthylimine*, a yellow, crystalline powder, m. p. $141-143^\circ$. *Triphenylphosphinebenzoylimine*, colourless crystals, m. p. $193-194^\circ$, which is unusually stable and exhibits very feebly basic properties. *Phenyldiethylphosphinephazide*, NPh:N:N:PPhEt_2 , a pale yellow, crystalline powder, m. p. $51-52^\circ$ (decomp.). *Phenyldiethylphosphinephenylimine*, NPh:PPhEt_2 , a colourless, crystalline powder, m. p. $69-70^\circ$,

which has only feebly basic properties. *Phenyldiethylphosphinebenzoylimine*, colourless crystals, m. p. 73–74°, which decomposes into phenyldiethylphosphine oxide and benzonitrile when distilled. *Triethylphosphineimine azide*, $\text{PEt}_3\cdot\text{NH}_3\text{N}_3\text{H}$ (from triethylphosphine and hydrogen azide in light petroleum solution). *Triethylphosphinemethylimine*, $\text{NMe}\cdot\text{PEt}_3$, a colourless liquid, b. p. 94–96°, which is extremely sensitive to moisture. *Triethylphosphineethylimine*, a colourless liquid, b. p. 93.5°/11 mm., is highly reactive towards unsaturated compound; with carbon dioxide or ethyl thiocarbimide it gives *diethylcarbodi-imide*, $\text{NEt}\cdot\text{C}\cdot\text{N}\cdot\text{Et}$, a colourless liquid, b. p. 24.5°/11 mm. *Triethylphosphinephenylimine*, a pale yellow, oily liquid, b. p. 116°/0.08 mm. *Triethylphosphinebenzoylimine*, colourless crystals, m. p. 62.5–63°. Boiling triethylphosphine is readily acted on by nitrous oxide with formation of triethylphosphine oxide and nitrogen. *Triisooamylphosphine*, b. p. 131–132°/11 mm., combines with phenyl azide to yield *triisooamylphosphinephenylphosphazide*, $\text{P}(\text{C}_5\text{H}_{11})_3\cdot\text{N}\cdot\text{N}\cdot\text{NPh}$, a yellow, crystalline precipitate, m. p. 57–58°, which decomposes readily with formation of *triisooamylphosphinephenylimine*, a colourless liquid, b. p. 161°/0.04 mm. *Triisooamylphosphineethylimine*, a colourless liquid, b. p. 119°/0.23 mm.; the immediately formed phosphazide appears to be relatively stable, but it was not isolated. H. W.

Organic Compounds of Phosphorus. V. Action of Carbonylene Derivatives on Phosphazines. H. STAUDINGER and W. BRAUNHOLTZ (*Helv. Chim. Acta*, 1921, 4, 897–900).—It has been shown previously that phosphineimine derivatives, phosphinemethylene derivatives, and phosphine sulphides react with carbonylene or thiocarbonylene compounds to give phosphine oxides and substances of the types $\text{R}\cdot\text{N}\cdot\text{C}\cdot\text{X}$, $\text{CR}_2\cdot\text{C}\cdot\text{X}$, and $\text{S}\cdot\text{C}\cdot\text{X}$ respectively, and that the compounds just named are particularly reactive (cf. Staudinger and Meyer, A., 1920, i, 106; Staudinger, Rathsam, and Kjelsberg, A., 1921, i, 33). The work has now been extended to the phosphazines, but the results are generally unsatisfactory.

Triphenylphosphinebenzophenoneazine reacts readily with phenylcarbimide, but the primary product polymerises rapidly to a colourless product of high molecular weight which evolves phenylcarbylimine freely when heated. Reaction appears to occur thus: $\text{PPh}_3\cdot\text{N}\cdot\text{N}\cdot\text{CPh}_2 + \text{O}\cdot\text{C}\cdot\text{NPh} \rightarrow \text{PPh}_3\text{O} + (\text{CPh}_2\cdot\text{N}\cdot\text{N}\cdot\text{C}\cdot\text{NPh})$ (not N_2 ; $\text{CPh}_2\cdot\text{C}\cdot\text{NPh} + \text{N}_2$) \rightarrow polymeride $\rightarrow \text{C}\cdot\text{NPh} + (?)\text{CPh}_2\cdot\text{N}\cdot\text{N}$. Reaction proceeds similarly, but more slowly, with phenylthiocarbimide. With carbon disulphide the phosphazine gives polymerides of high molecular weight, which could not be purified instead of the desired compound, $\text{CPh}_2\cdot\text{N}\cdot\text{N}\cdot\text{C}\cdot\text{S}$, which might decompose into nitrogen and $\text{CPh}_2\cdot\text{C}\cdot\text{S}$. Carbon dioxide reacts very slowly with the phosphazine and does not appear to give diphenylketen. Sulphur dioxide gives a well-defined additive compound with triphenylphosphinebenzophenoneazine, from which the unchanged phosphazine can be regenerated by very cautious heating; at a slightly higher temperature, fission of the phosphazine

occurs with evolution of nitrogen and formation of triphenylphosphine oxide, benzophenone, and sulphur, probably in accordance



with the scheme: $\begin{array}{c} \text{O} \\ | \\ \text{O} \cdots \text{S}:\text{O} \end{array}$
 $\rightarrow \text{CPh}_2\text{S}:\text{O} \rightarrow \text{CPh}_2\text{O} + \text{S}$. The reaction is highly complicated, since the phosphine sulphide and small amounts of thiobenzophenone are also produced. A complex change takes place also with thionylaniline, yielding the phosphine oxide and sulphide and an oil which gives benzophenone and many other products when heated.

H. W.

Organic Compounds of Arsenic. VI. Fission of Alkylated or Arylated Arsine Hydroxybromides.

WILHELM STEINKOPF and GUSTAV SCHWEN (*Ber.*, 1921, 54, [B], 2802—2811).—Under the influence of heat, the hydroxy-bromides of tertiary arsines suffer, in part, decompositions analogous to those experienced by the trialkylhalogenoammonium hydroxides and on this account appear to have the constitution $[\text{AsR}_3\text{Br}]\text{OH}$. On the other hand, their complete hydrolysis to trialkyl-(aryl)arsine oxides or their hydroxide and the pyrogenic fission to alkyl bromide and aryl and dialkyl-(aryl)-arsenious acid are more readily expressed by the formula $[\text{AsR}_3\text{OH}]\text{Br}$. The formulation with quinequivalent arsenic, $\text{AsR}_3\text{Br}\cdot\text{OH}$, gives a formal picture, but not an explanation of their reactions.

Phenyldimethylarsine hydroxybromide is decomposed when heated at 160—180° in a vacuum into phenyltrimethylarsonium bromide and phenylmethylarsenic acid, which remain in the flask, a distillate of higher boiling point which is converted by being heated with methyl iodide into phenyltrimethylarsonium iodide, phenyltrimethylarsonium tri-iodide, and (?) phenyldibromoarsine [which thus in accordance with the observations of Steinkopf and Schwén (A., 1921, i, 694) must contain phenyldimethylarsine and phenylmethylbromoarsine], and a distillate of lower boiling point containing methyl bromide, water, and methyl alcohol. Fission under atmospheric pressure at about 195° gives a distillate containing methyl bromide, methyl alcohol, and aqueous hydrobromic acid and a residue consisting of arsenious acid and phenyltrimethylarsonium bromide which are insoluble in ether together with phenyldimethylarsine and phenylmethylbromoarsine and diphenylbromoarsine, which dissolve in ether and are transformed by methyl iodide into phenyltrimethylarsonium iodide and tri-iodide, diphenyldimethylarsonium tri-iodide, and diphenyliodoarsine. The changes are represented by the schemes: (1) $\text{AsPhMe}_2\text{Br}\cdot\text{OH} \rightarrow \text{AsPhMe}_2 + \text{HBr} \rightarrow \text{HBr} + \text{O}$; (2) $\text{AsPhMe}_2\text{Br}\cdot\text{OH} \rightarrow \text{AsPhMeBr} + \text{MeOH}$; (3) $2\text{AsPhMe}_2\text{Br}\cdot\text{OH} \rightarrow 2\text{MeBr} + 2\text{AsPhMe}\cdot\text{OH} \rightarrow (\text{AsPhMe})_2\text{O} + \text{H}_2\text{O}$. The phenyldimethylarsine oxide reacts with the liberated hydrogen bromide thus, $(\text{AsPhMe})_2\text{O} + 2\text{HBr} \rightarrow 2\text{AsPhMeBr} + \text{H}_2\text{O}$, whereas the phenyltrimethylarsonium bromide is a secondary product derived from methyl bromide and phenyldimethylarsine. The changes (1) and

(2) are similar to those suffered by trialkylhalogenoammonium hydroxides.

Triphenylarsine hydroxy-bromide is decomposed in a vacuum at about 250°, giving two distillates, the more volatile of which contains bromobenzene, water, and hydrobromic acid, whereas the less volatile is a mixture of bromobenzene, triphenylarsine, and diphenylbromoarsine, since it is converted by methyl iodide into triphenylmethylarsonium tri-iodide and diphenyldimethylarsonium tri-iodide. The presence of phenol could not be established. Fission, which is not quantitative, occurs in accordance with the schemes: $\text{AsPh}_3\text{Br}\cdot\text{OH} \rightarrow \text{AsPh}_3 + \text{HOBr} \rightarrow \text{HBr} + \text{O}$ and $\text{AsPh}_3\text{Br}\cdot\text{OH} \rightarrow 2\text{PhBr} + \text{H}_2\text{O} + (\text{AsPh}_3)_2\text{O} \xrightarrow{2\text{HBr}} 2\text{AsPh}_2\text{Br} + \text{H}_2\text{O}$.
H. W.

Organic Compounds of Arsenic. V. Action of Cyanogen Bromide on Phenylated Tertiary Arsines. WILHELM STEIN-KOPF and GUSTAV SCHWEN (*Ber.*, 1921, 54, [B], 2791—2801; cf. A., 1921, i, 694).—Phenylated tertiary arsines unite with cyanogen bromide in much the same manner as do the trialkylarsines (Steinkopf and Müller, A., 1921, i, 404) to give cyanobromides which undergo normal fission into alkyl haloid and cyanoarsine except in the case of triphenylarsine cyanobromide, the decomposition of which follows a complex course, leading, in part, to regeneration of the initial material. The ability of the di- and tri-phenylarsines to form bromocyanides, whereas the corresponding amines appear to be indifferent towards cyanogen bromide, is attributed to the more positive character of the arsenic atom.

Phenyldimethylarsine bromocyanide, $\text{AsPhMe}_2\text{Br}\cdot\text{CN}$, a colourless, microcrystalline powder, m. p. 94—96°, is prepared by the gradual addition of a solution of bromocyanogen in dry light petroleum to phenyldimethylarsine dissolved in the same medium, the apparatus used being that described by Wolfram (A., 1921, ii, 395). It is converted by moisture into *phenyldimethylarsine hydroxy-bromide*, $\text{AsPhMe}_2\text{Br}\cdot\text{OH}$, lustrous needles, m. p. 162°, which is converted by silver oxide into *phenyldimethylarsine dihydroxide*. The latter is transformed readily into *phenyldimethylarsine hydroxy-chloride*, colourless needles, m. p. 163°, *phenyldimethylarsine hydroxy-picrate*, needles, m. p. 132°, and *phenyldimethylarsine hydroxy-iodide*, yellow needles, m. p. 117°. *Phenyldimethylarsine iodocyanide*, yellow, crystalline powder, m. p. 93°, is prepared from its components and is converted by moisture into the hydroxy-iodide just described. Phenyldimethylarsine bromocyanide is decomposed by heat into *cyanophenylmethylarsine*, $\text{AsPhMe}\cdot\text{CN}$, b. p. 127°/11 mm.

Diphenylmethylarsine bromocyanide, $\text{AsPh}_2\text{MeBr}\cdot\text{CN}$, a colourless, voluminous, crystalline powder, m. p. 61—62°, is prepared from its components; it is converted by moisture into *diphenylmethylarsine hydroxy-bromide*, transparent crystals, m. p. 118° (corresponding *picrate*, m. p. 137°). The bromocyanide is converted by heat into methyl bromide and *diphenylcyanoarsine*, $\text{AsPh}_2\cdot\text{CN}$, m. p. 31·5°, b. p. 191°/11 mm.

Triphenylarsine bromocyanide, colourless, relatively coarsely

crystalline powder, m. p. (indefinite) 130—140° after softening at 120°, is converted by moisture into triphenylarsine hydroxybromide, m. p. 168° (corresponding *picrate*, yellow needles, m. p. 162—163°). H. W.

Aromatic Arsenic Compounds. IX. Diazoamino-compounds of *p*-Aminophenylarsinic Acid and its Derivatives.

WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1921, **43**, 1632—1645; cf. *A.*, 1920, i, 107, 108, 110, 111, 114, 116, 117).—It has previously been observed by Ehrlich and Bertheim that *p*-aminophenylarsinic acid can be diazotised and the resulting diazo-compound coupled without difficulty, yielding azo-dyes (cf. *A.*, 1907, i, 812). The authors now show that this reaction can be extended to the preparation of well-defined diazo-amino-compounds containing the arsenic acid residues, and several such groups of compounds have been prepared and are described. For the treatment of experimental trypanosomiasis these compounds possess certain inherent disadvantages, and their use has been discontinued. The following compounds are described.

Diazobenzene(4-arsinic acid)dimethylamine, m. p. 182° (decomp.), giving a sodium salt; *diazobenzene(4-arsinic acid)diethylamine*, m. p. 195—200° (decomp.), and its sodium salt; *diazobenzene(4-arsinic acid)piperidine*, m. p. 162—163°, and its sodium salt; *bisdiazobenzene(4-arsinic acid)pentamethylenetetramine*, m. p. 210—212° (decomp.), and its sodium salt.

Diazobenzene(4-arsinic acid)aniline, m. p. 112—113° (decomp.), and its sodium salt; *diazobenzene(4-arsinic acid)methylaniline*, m. p. 160—162° (decomp.), and its sodium salt; *diazobenzene(4-arsinic acid)-p-toluidine*, m. p. 130—132°, and its sodium salt; *diazobenzene(4-arsinic acid)-4'-chloroaniline*, m. p. 177° (decomp.), and its sodium salt; *diazobenzene(4-arsinic acid)-o-anisidine*, m. p. 95—99° (decomp.), and its sodium salt; *diazobenzene(4-arsinic acid)-p-anisidine*, m. p. 116—119° (decomp.), and its sodium salt; *diazobenzene(4-arsinic acid)-4'-aminoacetanilide*, m. p. 165—170° (decomp.), and its sodium salt; *diazobenzene(4-arsinic acid)-4'-aminophenol*, its benzoic ester, m. p. 155—158° (decomp.), and its sodium salt; *diazobenzene(4-arsinic acid)-4'-aminoacetophenone*, m. p. 177—178° (decomp.), and its sodium salt.

Diazobenzene(4-arsinic acid)-o-aminobenzoic acid, m. p. 160° (decomp.), and its mono- and di-sodium salts; *diazobenzene(4-arsinic acid)-m-aminobenzoic acid*, m. p. 141°, and its mono- and di-sodium salts; *diazobenzene(4-arsinic acid)-p-aminobenzoic acid*, and its monosodium salt; *methyl diazobenzene-4-arsinic acid-3'-amino-6'-methoxybenzoate*, m. p. 90—95° (decomp.), and the free acid, m. p. 140° (decomp.), and its disodium salt; *diazobenzene(4-arsinic acid)-3'-aminoanisic acid*, m. p. 150—155° (decomp.), its methyl ester, m. p. 150° (decomp.), and its disodium salt; *methyl diazobenzene(4-arsinic acid)-6'-aminopiperonylate* and the corresponding sodium salt; *diazobenzene(4-arsinic acid)-4'-aminocinnamic acid*, m. p. 155—160° (decomp.), its ethyl ester, m. p. 155—160° (decomp.), its disodium salt, and the sodium salt of the ethyl ester;

diazobenzene(4-arsinic acid)-4'-aminophenylarsinic acid, m. p. 154° (decomp.), and its mono- and di-sodium salts.

Diazobenzene(4-arsinic acid)phenylglycine and its sodium salt; diazobenzene(4-arsinic acid)-p-tolylglycine, m. p. 148—149° (decomp.), and its sodium salt; diazobenzene(4-arsinic acid)benzylglycine, m. p. 155—160° (decomp.); diazobenzene(4-arsinic acid)-4'-methoxyphenylglycine, its sodium salt, its ethyl ester and the sodium salt of the ester; diazobenzene(4-arsinic acid)-4'-ethoxyphenylglycine, its sodium salt, its ethyl ester, and the sodium salt of the ester.

Diazobenzene(4-arsinic acid)-4'-aminophenoxyacetic acid, m. p. 132° (decomp.), its disodium salt, its ethyl ester, m. p. 132—133° (decomp.), and the sodium salt of the latter; the acetamide, m. p. 162° (decomp.), and its sodium salt, and the acetomethylamide, m. p. 170° (decomp.), and its sodium salt; diazobenzene(4-arsinic acid)-4'-methylaminophenoxyacetic acid, m. p. 155—160° (decomp.); diazobenzene(4-arsinic acid)-3'-methyl-4'-aminophenoxyacetic acid, its disodium salt, its methyl ester, and the sodium salt of the latter; diazobenzene(4-arsinic acid)-4'-amino-2'-methylphenoxyacetic acid, its disodium salt, its methyl ester, m. p. 143—144° (decomp.), and the sodium salt of the latter; methyl diazobenzene(4-arsinic acid)-4'-amino-2':5'-dimethylphenoxyacetate, m. p. 120° (decomp.), and the disodium salt of the free acid; methyl diazobenzene(4-arsinic acid)-4'-amino-2'-methyl-5'-isopropylphenoxyacetate, m. p. 145° (decomp.), and the disodium salt of the free acid; methyl diazobenzene(4-arsinic acid)-4'-amino-3'-methyl-6'-isopropylphenoxyacetate and the disodium salt of the free acid; diazobenzene(4-arsinic acid)-2'-bromo-4'-aminophenoxyacetic acid, m. p. 120° (decomp.), its methyl ester, m. p. 154—155° (decomp.), and its disodium salt; diazobenzene(4-arsinic acid)-6-bromo-4-amino-2-methylphenoxyacetic acid, m. p. 155° (decomp.), its disodium salt, and its methyl ester, m. p. 188° (decomp.); diazobenzene(4-arsinic acid)-4'-amino-6'-acetophenoxyacetic acid, its disodium salt, and its methyl ester, m. p. 155° (decomp.); 6-diazo-o-toluene(3-arsinic acid)-p-aminophenoxyacetic acid, its disodium salt, and its methyl ester, m. p. 130—132° (decomp.); diazo-2-bromobenzene(4-arsinic acid)-p-aminophenoxyacetic acid, m. p. 130° (decomp.), its disodium salt, its methyl ester, m. p. 123—125° (decomp.), and the sodium salt of the ester. W. G.

Aromatic Arsenic Compounds. X. Azo-dyes derived from p-Aminophenylarsinic Acid. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1921, **43**, 1646—1654; cf. preceding abstract).—It has been found that certain classes of aromatic amino-compounds yield aminoazo-dyes at once when coupled with diazotised arsanilic acid or give diazoamino-compounds which rapidly undergo rearrangement, giving the dyes. In most cases the reaction between the amino-compound and the diazotised arsanilic acid proceeded smoothly, but the isolation and purification of the resulting dyes was often difficult. The following compounds are described:—

1-Amino-2-methoxynaphthalene-4-azobenzene-4'-arsinic acid; 1.

amino-4-methoxynaphthalene-2-azobenzene-4'-arsinic acid, m. p. 195° (decomp.).

4-Methylamino-5-carboxybenzeneazobenzene-4'-arsinic acid and its mono- and di-sodium salts; 4-ethylamino-5-carboxybenzeneazobenzene-4'-arsinic acid and its monosodium salt; 4-isoamylamino-5-carboxybenzeneazobenzene-4'-arsinic acid, its hydrochloride, and its monosodium salt; 4-amino-2:3-dimethoxy-5-carboxybenzeneazobenzene-4'-arsinic acid, its hydrochloride, and its monosodium salt; 2-amino-4:5-dimethoxy-3-carboxybenzeneazobenzene-4'-arsinic acid, its hydrochloride, and its monosodium salt.

4-Benzene(4'-arsinic acid)azo-phenylglycine, m. p. 170—175° (decomp.), and its hydrochloride; 4-benzene(4'-arsinic acid)azo-2-methylphenylglycine, m. p. 157° (decomp.), and its hydrochloride; 4-benzene(4'-arsinic acid)azo-2-methoxyphenylglycine, m. p. 167° (decomp.), and its sodium salt; 4-benzene(4'-arsinic acid)azo-2-ethoxyphenylglycine, m. p. 245—250° (decomp.), and its sodium salt; *z'*-benzene(4'-arsinic acid)azo-*z*-naphthylglycine, m. p. 275° (decomp.), and its disodium salt.

4-Benzene(4'-arsinic acid)azo-phenylaminomethanesulphonic acid, $\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{SO}_3\text{H}$, m. p. 187—189°, and its disodium salt; 4-benzene(4'-arsinic acid)azo-2-methoxyphenylaminomethanesulphonic acid, m. p. 158—160° (decomp.), and its disodium salt.

6-Benzene(4'-arsinic acid)azo-3-aminophenoxyacetic acid, $\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, its hydrochloride, and its monosodium salt; 6-benzene(4'-arsinic acid)azo-3-amino-4-methylphenoxyacetic acid, m. p. 242—243° (decomp.), its hydrochloride, and its monosodium salt; 4-benzene(4'-arsinic acid)azo-5-amino-2-methylphenoxyacetic acid, m. p. 187—188° (decomp.), its hydrochloride, and its monosodium salt; 4-benzene(4'-arsinic acid)azo-3-amino-6-methoxyphenoxyacetic acid, and its hydrochloride; 4-amino-6-methoxy-3-[phenyl-(4'-arsinic acid)azo]-phenoxyacetic acid, its hydrochloride and its monosodium salt; 5-benzene(4'-arsinic acid)azo-4-amino-1:2-bisphenoxyacetic acid, and its monosodium salt; β -benzene(4'-arsinic acid)azo-*z*-amino-*z'*-naphthoxyacetic acid, m. p. 285° (decomp.), and its disodium salt; *z'*-benzene(4'-arsinic acid)azo-*z*-amino- β -naphthoxyacetic acid and its disodium salt; 5-benzene(4'-arsinic acid)azo-2-hydroxy-phenoxyacetic acid and its monosodium salt.

W. G.

Preparation of Dimethyl- and Diphenyl-arsinecarboxylic Acids. ANDRÉ JOB and HENRI GUINOT (Fr. Patents 521119 and 521469; from *Chim. Zentr.*, 1921, iv, 870—871).—Cacodyl cyanide, AsMe_2CN , and diphenylarsine cyanide, AsPh_2CN , respectively, are submitted to hydrolysis by the usual methods for the preparation of carboxylic acids from nitriles. By hydrolysis of cacodyl cyanide with dilute sulphuric acid and subsequent neutralisation with calcium hydroxide, the calcium salt of dimethylarsinecarboxylic acid is obtained, from which the free acid, $\text{AsMe}_2\text{CO}_2\text{H}$, is formed by decomposition with acids and recrystallisation from an appropriate solvent. It reddens blue litmus and gives stable salts with

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a number of common metals and alkaloids. *Diphenylarsinecarboxylic acid*, $\text{AsPh}_2\text{CO}_2\text{H}$, is similarly prepared. By treatment of diphenylarsine cyanide with hydrogen peroxide or substances forming hydrogen peroxide, *diphenylarsinoformamide*,
 $\text{AsPh}_2\text{CO}\cdot\text{NH}_2$,

is formed with evolution of oxygen and may be obtained by crystallisation from suitable solvents. It is decomposed by nitrous acid, giving nitrogen and diphenylarsinecarboxylic acid. G. W. R.

Organo-chromium Compounds. II. Abnormal Salt Formation of Chromium Pentaphenyl Hydroxide. Chromium Tetraphenyl Salts (Elimination of a Phenyl Group). FRANZ HEIN (*Ber.*, 1921, 54, [B], 2708—2727; cf. A., 1921, i, 826).—It has been shown previously that chromic chloride or chromyl chloride is converted by magnesium phenyl bromide in cold ethereal solution into a mixture of bromides from which chromium pentaphenyl bromide can be isolated in small amount and in an impure state; the most definite compound of the series is chromium pentaphenyl hydroxide, $\text{CrPh}_5\cdot\text{OH}\cdot 4\text{H}_2\text{O}$. Attempts to isolate the pure pentaphenyl salts by the action of acids or salts on the crystalline base lead in a surprising manner to the loss of a phenyl group and formation of chromium tetraphenyl salts, the only exception to this regularity being found in the production of the pentaphenyl carbonate. The tetraphenyl salts, in so far as they are soluble in a mixture of alcohol and water, yield neutral solutions and are therefore not hydrolysed. Their normal behaviour is shown by the observation that the haloids give immediate precipitates with silver nitrate solution, and, with suitable acids, give precipitates of the corresponding sparingly soluble chromium tetraphenyl salts. They have also a marked tendency towards the formation of complex salts and polyiodides. Attempts to isolate chromium tetraphenyl hydroxide by the electrolysis of an alcoholic solution of the iodide were only partly successful. The author considers that the phenyl group is liberated in the nascent condition; it is present in the solutions largely in the form of phenol (the formation of which is attributed to the action of dissolved or atmospheric oxygen and, to some extent of water), of diphenyl and of a solid acidic substance which could not be characterised completely.

The action of a freshly-prepared, very dilute alcoholic solution of chromium pentaphenyl hydroxide on a dilute, aqueous alcoholic solution of Reinecke's salt leads to the precipitation of *chromium tetraphenylchromitetraethiocyanatodiammine*, $\text{Ph}_4\text{Cr}\left[\text{Cr}\left(\begin{smallmatrix} \text{CNS} \\ \text{NH}_2 \end{smallmatrix}\right)_4\right]$, thin, golden-yellow leaflets, m. p. 173° (decomp.), when placed in a bath at 165° . The salt is also obtained from the β -modification of the base. It is somewhat sensitive to rise in temperature and to prolonged desiccation over concentrated sulphuric acid. It is extraordinarily stable when preserved beneath alcohol or mixtures of alcohol and water. Determinations of the molecular weight in freezing nitrobenzene indicate extensive dissociation, which is presumably ionic in character. A compound of chromium tetra-

phenyl iodide with chloroform, $\text{CrPh}_4\text{I} \cdot \text{CHCl}_3$, dark brownish-red, rhombic leaflets, is prepared conveniently by agitating the base with hydriodic acid or aqueous potassium iodide solution and chloroform, and is isolated from the chloroform extract. If the latter is treated with two to three times its volume of ether, a second salt $(+\frac{1}{2}\text{CHCl}_3)$ separates. The solvent can be removed by gentle heating, leaving *chromium tetraphenyl iodide*, m. p. 178° (decomp.), after being placed in a bath at $165\text{--}170^\circ$. The salt appears to be somewhat associated in boiling chloroform, but dissociated in freezing phenol. It forms complex salts with silver iodide or mercuric chloride, which, however, are remarkably less stable than the parent substance. It gives a *periodide*, CrPh_4I_5 , chocolate-brown prisms, when its solution in alcohol or chloroform is slowly added to an alcoholic solution of iodine. *Chromium tetraphenyl bromide* is prepared in the same manner as the iodide; it forms orange-coloured, rectangular platelets $(+\frac{1}{2}\text{CHCl}_3)$ which readily loses the chloroform and then has m. p. 136° , and is considerably less stable than the corresponding iodide. *Chromium tetraphenyl perchlorate*, $\text{CrPh}_4\text{ClO}_4$, is prepared from the pentaphenyl base and perchloric acid in aqueous alcoholic solution; it forms orange-red crystals which are very unstable when dry and explode when gently warmed or lightly struck. *Chromium tetraphenyl dichromate*, $(\text{CrPh}_4)_2\text{Cr}_2\text{O}_7$, golden-orange leaflets, is most conveniently prepared by mixing solutions of the base and ammonium dichromate in methyl alcohol; it is somewhat unstable and decomposes in a few days when exposed to the air or preserved over calcium chloride, very readily in the presence of phosphoric oxide. It explodes when heated.

Chromium pentaphenyl carbonate, $(\text{CrPh}_5)_2\text{CO}_3 \cdot 6\text{H}_2\text{O}$, orange-coloured leaflets, is most readily prepared by the preservation of the concentrated aqueous mother-liquors from the preparation of the base exposed to air and in an ice-chest. It has m. p. (indefinite) $118\text{--}119^\circ$, after softening at about 108° when placed in a bath pre-heated at 95° . A *dihydrate* and a *monohydrate* are also described.

H. W.

Organo-chromium Compounds. III. Chromium Triphenyl Hydroxide and its Salts. FRANZ HEIN (*Ber.*, 1921, **54**, [B], 2727—2744; cf. A., 1921, i, 826 and preceding abstract).—Further examination of the solution of bases obtained by the action of silver oxide on the chromium polyphenyl bromide has disclosed the presence of chromium triphenyl hydroxide which remains dissolved after the separation of chromium pentaphenyl hydroxide. It is characterised by its extreme solubility in water. The solutions leave a strongly alkaline, syrupy, transparent, reddish-black mass when evaporated. In general, they are very unstable when highly concentrated, but may be preserved almost indefinitely when dilute and in the absence of light and air. Characteristic precipitates are obtained by the addition of many mineral acids or their alkali salts, but these are generally amorphous; it is remarkable that their colour resembles closely that of the corre-

sponding tetra- and penta-phenyl compounds. The most characteristic salt is *chromiumtriphenylchromitetra-thiocyanatodiammine*, $\text{CrPh}_3\left[\text{Cr}\frac{(\text{NH}_3)_2}{(\text{SCN})_4}\right]$, which is prepared by adding an aqueous alcoholic solution of Reinecke's salt to a similar solution of the base, until the precipitate commences to become distinctly flocculent, filtering and adding an excess of Reinecke's salt to the filtrate. The second amorphous precipitate becomes microcrystalline when preserved beneath the mother-liquor. It is preferably preserved beneath alcohol, when it remains unchanged for a long period, whereas, when washed with alcohol and ether and left exposed to air, it becomes discoloured and has an odour of diphenyl after three to four days. It crystallises with $2\text{H}_2\text{O}$, of which approximately $\frac{1}{2}$ molecule is lost on exposure to air, whereas a molecule is lost when it is dried immediately after its preparation over concentrated sulphuric acid. The monohydrate loses a further quantity of water when preserved over concentrated sulphuric acid, but decomposition occurs simultaneously. If, however, the freshly-prepared dihydrate is exposed to air in the absence of light and warmth for one to one and a half days and is then placed in a vacuum over concentrated sulphuric acid, it rapidly becomes completely dehydrated, giving a salt which can be preserved unchanged in the absence of air for a few hours, but which decomposes rapidly on exposure to air. The monohydrate and dihydrate have m. p. 168° when placed in a bath pre-heated to 155° . Like the corresponding tetraphenyl compound, they are transformed by great pressure into a viscous, resin-like mass. Determinations of the molecular weight of the dihydrate in freezing nitrobenzene gave abnormally low results, which are explained by the loss of one molecule of water; under similar conditions, the monohydrate behaves as if very extensively dissociated electrolytically.

Chromium triphenyl iodide, $\text{CrPh}_3\text{I}\cdot\text{Et}_3\text{O}$, is prepared by the addition of potassium iodide or hydriodic acid to an aqueous solution of the base in the presence of chloroform, into which the iodide passes. The concentrated chloroform solution is poured, after being dried, into ether; the iodide is thereby precipitated initially as an oil which gradually becomes solid. The hygroscopic salt can be preserved for a considerable period in a vacuum over concentrated sulphuric acid, but is unstable in the presence of dry or moist air. Like the corresponding tetraphenyl compound, the salt gives an amorphous additive compound with mercuric chloride and an amorphous periodide.

Chromium triphenyl perchlorate, $\text{CrPh}_3(\text{ClO}_4)_3$, can be prepared in the microcrystalline form by the fractional precipitation of a solution of chromium triphenyl hydroxide with dilute perchloric acid. It is preferably preserved in an ice-chest under a mixture of alcohol and ether; in the dry state, it is more labile and explosive than the corresponding tetraphenyl compound.

The results described in this and the preceding communication show that chromium pentaphenyl and triphenyl bromides are present in the "crude bromide." The latter greatly predominates

when the original action is too prolonged or when the temperature is allowed to rise; both bromides, however, appear to be primary products. In addition, small amounts of chromium phenyl compounds are formed which are insoluble in alcohol but readily soluble in chloroform to intensely olive-green solutions. They appear to be highly complex, probably containing several chromium atoms with differing valency within the molecule. They are formed invariably by the auto-decomposition of the orange chromium phenyl compounds, particularly when the process is oxidative. This fact appears to explain the greater extent of their formation when chromyl chloride in place of chromic chloride is treated with magnesium phenyl bromide.

H. W.

Physiological Chemistry.

Subcutaneous Absorption of Oxygen in Mountain Climbing and Aviation. RAOUL BAYEUX (*Compt. rend.*, 1921, **173**, 937—939).—The resistance to subcutaneous injection of oxygen diminishes as the height increases in the ascent of a mountain. That this is not due to the fatigue of climbing is shown by experiments conducted in a decompression chamber. In the latter experiment, the decrease in resistance was accompanied by a slight increase in the beat of the pulse and a very slight increase in the velocity of respiration. The reverse process occurs as the altitude decreases or the pressure in the chamber increases. The injection of oxygen was not accompanied by formation of a gaseous tumour and the oxygen was rapidly absorbed.

W. G.

Influence of Temperature on the Reaction of the Blood. JOSÉ M. DE CORRAL (*Biochem. Z.*, 1921, **117**, 1—9).—The reaction of blood at 38° is $P_{H_2} = 0.22$ lower than at 18°, in agreement with Michaelis and Davidoff's findings (*A.*, 1912, ii, 1184), provided that the blood is in equilibrium with carbon dioxide at 38° and then measured at 18°. If the blood is in equilibrium with carbon dioxide at both temperatures, then the P_{H_2} is independent of temperature as found by Hasselbalch (*A.*, 1917, i, 490). The results with serum still show discrepancies.

H. K.

Excretion of Sweat and the Composition of the Blood. EBERHARD WILBRAND (*Biochem. Z.*, 1921, **118**, 61—66).—Heavy perspiration is followed by a thickening of the blood; parallel with this there is a loss of protein and sodium chloride from the serum. The residual (non-precipitable) nitrogen of the blood and the content of fat are unaltered.

H. K.

Concentration of the Blood. II. The Action of Diuretics of the Purine Group on the Exchange of Substances between the Tissues and the Blood. W. NONNENBRUCH (*Arch. exp. Path. Pharm.*, 1921, **91**, 332—341).—Theophylline, theocine, and

euphylline cause the blood to lose water, which is soon replaced. The serum proteins increase often to a very large extent, not only relatively, but absolutely, and this stream of protein from the tissues into the serum even occurs after extirpation of the kidneys.
G. B.

An Effect of the Ingestion of Colostrum on the Composition of the Blood of New-born Calves. PAUL E. HOWE (*J. Biol. Chem.*, 1921, 49, 115—118).—The blood of the new-born calf does not contain euglobulin or pseudo-globulin I, but after ingestion of colostrum relatively large amounts of these proteins are present. If no colostrum is given, they are only formed slowly. The function of colostrum seems to be to supply them rapidly.
G. B.

Calcium Content of Blood Plasma and Corpuscles in the New-born. MARTHA R. JONES (*J. Biol. Chem.*, 1921, 49, 187—192).—The whole blood contains 8.8 mg., the corpuscles 5.0 mg., the plasma 12.3 mg. of calcium per 100 c.c. The average for plasma is higher and for corpuscles and whole blood less than for older children. In the first twelve days of life, the average percentage of red cells dropped from 55 to 42%.
G. B.

Action of Pilocarpine on the Composition of the Blood. A. BORNSTEIN and ROBERT VOGEL (*Biochem. Z.*, 1921, 118, 1—14).—Pilocarpine administered to dogs alters the distribution of water in the body, the blood showing increased content of hæmoglobin, corpuscles, and serum proteins. This change is only partly to be attributed to excretion of water from the body. In addition, pilocarpine produces hyperglycæmia in dogs and rabbits. Extirpation of the pancreas has no inhibiting action on these results, but atropine is antagonistic to all.
H. K.

Blood and Metabolism Studies with Radium Emanations. J. HAUSENSTEIN (*Munch. med. Woch.*, 1921, 68, 809—810; from *Chem. Zentr.*, 1921, iii, 795).—Observations were made of the effect of radium radiations on the numbers of red and white blood corpuscles and on the behaviour of the individual leucocyte forms in cases of carcinoma of the uterus. Red corpuscles disintegrate and decrease in amount under the influence of γ -rays. Leucocytes increase in number. There is a relative and absolute increase in neutrophils and a relative although not absolute decrease in lymphocytes. No effect was observed on the large, white blood cells, and the mononuclear, eosinophile, and basophile cells.

The metabolism experiments showed that the nitrogen content of the urine decreased markedly during and after treatment. Similar results were obtained for uric acid. Acetone and acetoacetic acid were not found. The figures for indican were abnormal and slight albuminuria was observed.
G. W. R.

Permeability of the Red Corpuscles of Human Blood for Anions. ERNST WIECHMANN (*Pflüger's Archiv*, 1921, 189, 109—125; from *Chem. Zentr.*, 1921, iii, 895).—In native human blood the chlorine ion is distributed between corpuscles and plasma in

the ratio 1 : 2.1. This distribution is unaltered by isotonic sodium chloride solution. In the presence of sodium sulphate solution, chlorine ions pass out from the corpuscles. The partition ratio between corpuscles and suspending liquid is found to be 1 : 19.7 for the sulphate ion, 1 : 9.7 for the phosphate ion, and 1 : 3.1 for the bromine ion and the chlorine ion, under similar conditions of experiment. The permeability for the phosphate ion increases with the temperature. Permeability for the bromine ion is decreased by the presence of calcium. "Cyanol," "light green-F.S.," "setopalm," and "ponceau 2R" were scarcely absorbed after two hours.

G. W. R.

Quinine Hæmolysis. ALFRED LUGER (*Biochem. Z.*, 1921, 117, 145—152).—When treated with quinine, blood corpuscles show a diminished resistance to acids and an increased resistance to alkalis. In the presence of saline solution, such corpuscles show a diminished resistance to water, but an increased resistance to saponin.

H. K.

The Amino-acid Content of Plasma and Corpuscles according to Bang. A. COSTANTINO (*Biochem. Z.*, 1921, 117, 140—144).—Polemical against I. Bang (cf. *A.*, 1916, i, 528).

H. K.

Normal Sugar Content of the Blood. P. J. CAMMIDGE, J. A. C. FORSYTH, and H. A. HOWARD (*Brit. Med. J.*, 1921, ii, 586—590).—As the result of observations on the blood-sugar of man and animals, the authors hold the view that the liver contains a diastatic ferment the action of which is reversible. In the fasting state, the glycogenolytic activities of this enzyme are largely inhibited by an anti-ferment formed by the pancreas, the impermeability of the resting liver cells to sodium chloride, and the reaction of the blood and liver cells. After the taking of food, when acids enter the duodenum, the secretion formed stimulates the liver cells to produce bile, thus permitting the entrance of sodium chloride, which activates the diastatic ferment. At the same time, it causes a secretion of alkaline pancreatic juice which combines with the acid gastric contents, forming acid salts and sodium chloride, which pass to the liver and increase the activity of the diastatic ferment. It also interferes with the formation of the internal secretion of the pancreas, thus diminishing its inhibitory effect on glycogenolysis in the liver. Carbohydrates reaching the liver from the intestine or formed from proteins in the liver are converted into glycogen by the diastatic ferment, the efficiency of the process depending on the extent to which the glycogenolytic action of the enzyme is inhibited by the internal secretion of the pancreas. Unless the power of glycogen formation possessed by the liver is exceeded, sugar as such, or formed from starch in the intestine, does not pass into the general circulation or play any direct part in the rise of blood-sugar following food.

G. B.

Lactic Acid in the Blood of Dogs in Exercise. A. B. HASTINGS (*Proc. Soc. Exp. Biol. Med.*, 1921, 18, 306—307).—Severe exercise of short duration increases the lactic acid, but prolonged

moderate exercise decreases it. The significance of lactic acid as a primary factor in physiological fatigue not carried to exhaustion seems to be an open question (cf. similar results in man, Ryffel, A., 1910, ii, 325). G. B.

Distribution of Uric Acid in the Blood. R. C. THEIS and S. R. BENEDICT (*J. Lab. Clin. Med.*, 1921, 6, 680—683).—Uric acid was estimated in plasma and corpuscles in 104 cases, 51 of which showed equal distribution, 45 showed plasma uric acid greater than corpuscle uric acid, and 8 the converse. This relationship holds for oxalated and defibrinated blood, and does not depend on pathological conditions. G. B.

Use of Frogs to Demonstrate the Anticoagulating Action of Nucleic Acids. DOYON (*Compt. rend.*, 1921, 173, 1120—1122).—The frogs are decapitated and sixty drops of their blood allowed to drop into 0.5 c.c. of a solution containing 0.0033 gram of nucleic acid, 0.0025 gram of sodium carbonate, and 0.002 gram of sodium chloride. No coagulation occurs. Other experiments with frogs are described. W. G.

Changes in the Blood after Oral Administration of Sodium Chloride. G. SAMSON (*Biochem. Z.*, 1921, 118, 55—60).—Oral administration of sodium chloride is followed by increased sodium chloride content of the blood-serum, the major portion, however, passing into the tissues. There is also an increase of the protein content of the blood. H. K.

Are there Protective Enzymes against Polysaccharides? EMIL ABDERHALDEN (*Biochem. Z.*, 1921, 117, 161—165).—Mainly polemical against Herzfeld and Klinger (cf. A., 1921, i, 286). H. K.

The Fate of some Polysaccharides in the Digestive Tract of Mammals. TOMIHIDE SHIMIZU (*Biochem. Z.*, 1921, 117, 227—240).—Fæcal constituents are able to convert inulin, lichenin, and hemicellulose into acetic, propionic, and butyric acids. Lactic acid also appears. The agent is probably bacterial, as pure cultures, for example, *Bacillus coli*, *B. lactis*, *B. proteus*, and *B. subtilis*, have the same power. H. K.

Hydrolysis of some Polysaccharides (Inulin, Lichenin, and Hemicellulose) in the Digestive Tract of Mammals. TOMIHIDE SHIMIZU (*Biochem. Z.*, 1921, 117, 241—244).—Macerated gut or pancreas, separately or combined, failed to liquefy or produce reducing sugars from the polysaccharides named. H. K.

Cellulose Fermentation in the Paunch of the Ox and its Importance for Metabolic Experiments. W. KLEIN (*Biochem. Z.*, 1921, 117, 67—68).—A criticism of Krogh and Schmit-Jensen's results (*J. Physiol.*, 1921, Sept. 20) on the carbon dioxide-methane ratio, chiefly on the grounds of priority. H. K.

Basal Metabolism of Underweight Children. KATHARINE BLUNT, ALTA NELSON, and HARRIET CURRY OLESON (*J. Biol. Chem.*, 1921, **49**, 247—262).—The basal metabolism tends to be (up to 40%) higher than in the normal child. G. B.

Variations in Chloride-metabolism Due to Menstrual Processes. W. EISENHARDT and R. SCHAEFER (*Biochem. Z.*, 1921, **118**, 34—38).—As a rule, immediately before or during the menstrual period there is an increased content of chloride in the circulating blood, as estimated by Bang's micro-method. H. K.

Calcium and Phosphoric Acid Metabolism with Large Doses of Calcium and Sodium Phosphate. K. BLÜHDORN (*Z. Kinderheilk.*, 1921, **29**, 43—55; from *Chem. Zentr.*, 1921, iii, 886).—No harmful effects followed the administration of large quantities of calcium. A portion of the calcium given as chloride or lactate is probably retained, but the greater part is excreted in the feces. The phosphoric acid exchanges run parallel with the calcium exchanges. Addition of sodium phosphate increases the retention of calcium. When calcium chloride is administered, it is apparently retained as such at first. G. W. R.

Facilitation of Intermediary Sugar Metabolism. H. STAUB (*Biochem. Z.*, 1921, **118**, 93—102).—There is a diminished capacity for assimilating the first dose of dextrose in fasting persons, or after a diet of fat and protein, and also after hard work. In a fasting person, the assimilation increases to a maximum after ten hours, and then falls off after fifteen or more hours. To explain these and other results, "equilibrating ferments" (Gleichgewichtsfemente) are postulated as produced in the blood by foodstuffs to restore to equilibrium the sudden abnormal conditions produced by a high concentration of the food administered. H. K.

Influence of some Polysaccharides (Inulin, Lichenin, and Hemicellulose) on Protein Exchange. TOMIHIDE SHIMIZU (*Biochem. Z.*, 1921, **117**, 245—251).—Feeding experiments on dogs show that the polysaccharides named have a protein-sparing action. H. K.

The Fate of Parenteral Administered Sulphur and its Influence on Metabolism. ROBERT MEYER-BISCH and E. BASCH (*Biochem. Z.*, 1921, **118**, 39—49).—Intramuscular injection of sulphur in oil is followed by increased protein breakdown, shown by increased nitrogen and sulphur output in the urine, the proportion of the latter element being greater than that administered. H. K.

Antiketogenesis. III. Calculation of the Ketogenic Balance from the Respiratory Quotients. PHILIP A. SHAFFER (*J. Biol. Chem.*, 1921, **49**, 143—162; cf. A., 1921, i, 754).—The author makes the following assumptions (not wholly justified by experiment). (1) Each molecule of fat gives 3 molecules of acetoacetic acid and 0.5 molecule of dextrose, or its equivalent antiketogenic derivative. (2) Protein is convertible (a) into antiketogenic dextrose or its equivalent to the extent of 3.6 grams

for each gram of urine nitrogen, (b) into acetoacetic acid for each molecule of leucine, phenylalanine, and tyrosine, it being calculated that each gram of urine nitrogen corresponds with approximately 10 millimols. of ketogenic substance. (c) Valine, lysine, histidine, and tryptophan are neutral as to ketogenesis. (3) Carbohydrate exerts its antiketogenic function in the form of dextrose, 1 gram of which is therefore equivalent to $1000/180 = 5.56$ millimols. of antiketogenic substance.

A method is described by which the ratio of ketogenic to anti-ketogenic molecules in the metabolic mixture can be calculated from the respiratory quotient. The molecular ratio 1:1 corresponding according to the calculation with a respiratory quotient of 0.76, appears to be the limit for the avoidance of acetone substances. With a quotient >0.76 the katabolism of the antiketogenic dextrose or its equivalent from protein and glycerol is great enough to remove aceto-acetic acid as fast as it is formed.

G. B.

The Minimum of Odour Perceptible in an Absolutely Inodorous Space (Camera Inodorata). K. KOMURO (*Arch. Néerl. Physiol.*, 1921, 6, 20—24).—The camera is a large glass box which can be made inodorous by means of a mercury vapour lamp and into which the head of the experimenter can be introduced. Inside this chamber the minimum necessary for perception of a number of odours is 20—25% less than outside, that is, the nose becomes more sensitive when all other odours are eliminated.

G. B.

Acid Taste. WOLFGANG OSTWALD and ALFRED KUHN (*Kolloid Z.*, 1921, 29, 266—271).—The connexion between the acid taste and the power of producing swelling is considered. It is shown that neither quantity is strictly proportional to the free hydrogen-ion concentration, nor is this quantity in any way a quantitative measure of either. The stronger the swelling action of an acid, the greater the hydrogen-ion concentration must be before an acid taste is detectable. Consequently, swelling action and acid taste are directly opposed to one another. Strongly swelling acids taste less acid than weakly swelling acids of the same hydrogen-ion concentration. The series of minimum hydrogen-ion concentrations which can be detected by taste and the series of swelling constants do not run parallel for the 13 acids examined, but may be connected by means of an experimental equation which contains two constants. Acid salts and buffer solutions exhibit the above-named relationship between acid taste and swelling power. Solutions of these substances taste much more acid than solutions of their acids of the same hydrogen-ion concentration. This is in keeping with the colloid-chemical rule that the addition of salts reduces the swelling power of acids. A tentative hypothesis is put forward that the acid taste is qualitatively due to the hydrogen ion, but quantitatively to the simultaneous swelling action of the colloids in the region of the nerve-endings which is not determined by the hydrogen-ion concentration.

J. F. S.

Chemical Constituents of the Egg of the Common Frog (*Rana temporaria*) and their Rôle in its Embryonic Development. E. FAURÉ-FREMIET and (Mlle) DU VIVIER DE STREEL (*Bull. Soc. Chim. Biol.*, 1921, 3, 476—482).—The ripe egg has the following composition: water 57.60%, glycogen 3.31%, lipoids 10.14%, vitellin tablets 26.51%, the remaining 2.44% consisting of pigment, nucleus, and cytoplasm. The vitellin tablets, which are partly soluble in alkalis, contain phosphorus, nitrogen, and sulphur.
E. S.

Constitution of the Egg of *Sabellaria alveolata*, L. E. FAURÉ-FREMIET (*Compt. rend.*, 1921, 173, 1023—1026).—The eggs of *Sabellaria alveolata*, L., contain 70% of water; 19.08% of protein; 6.80% of fats and lipoids; 1.27% of glycogen, and 1.53% of ash. The protein fraction consists of two distinct substances, one slightly acid, the other neutral. The fatty substances in the eggs exist in three principal forms, namely, neutral fats, soaps, and phosphatides.
W. G.

Tetrodon Poison and some of its Chemical Characteristics. F. ISHIHARA (*Tōkyō Igakukai Zasshi*, 1917, 31, 1—39).—The poison, which was extracted from eggs of the globe fish, is a tasteless, white powder containing sulphur and an amino-group; it gives a positive ninhydrin reaction and a positive reaction for creatinine. Dextrose is present, probably as a dextrose ester.

CHEMICAL ABSTRACTS.

The Chemical Composition of Brain. TOMOHIDE SHIMIZU (*Biochem. Z.*, 1921, 117, 252—262).—From 35 kilos. of ox-brain, fractions of a gram of most of the amino-acids were isolated, together with purine and pyrimidine bases and choline. Non-nitrogenous constituents identified were succinic acid, *d*-lactic acid, and inositol.
H. K.

The Calcium-Potassium Action. K. SPIRO (*Schweiz. med. Woch.*, 51, 457—460; from *Chem. Zentr.*, 1921, iii, 888—889).—Examples are given of the antagonistic physiological action of calcium and potassium. With isolated frogs' hearts, poisoning by potassium salts was neutralised by calcium salts. The effect of certain alkaloids may be influenced by the relative amounts of calcium and potassium present. Changes in the reaction of the medium influence the calcium-potassium action.
G. W. R.

Choline as Hormone for Intestinal Movement. III. Participation of Choline in the Action of Various Organic Acids on the Intestine. IV. Effect of Choline on Normal Gastric Movement. J. W. LE HETX (*Pflüger's Archiv*, 1921, 190, 280—300, 301—310; cf. *Ann. Report*, 1919, 160).—III. The effect on the isolated intestines of salts of various organic acids is explained as being due to the formation from these acids of esters of choline from the choline present in the walls of the bowel, with the aid of a synthetic enzyme which is also there. The activity of these esters, compared with choline, as estimated by the contraction

produced, is: Acetic ester 1000, propionic 300, formic 100, *n*-butyric 40, isovaleric 15, benzoic 2, succinic 1. The sodium salts of the acids have no effect, if the intestine is first freed from choline by washing; in some cases the further addition of choline or of the washings restores the effect. Atropine antagonises the effect of these salts, as it does that of choline. The possibility that the stimulating effect of sugars on the intestine may be due to intermediate formation of a pyruvic ester is discussed. IV. X-Ray observations on cats showed that 4–10 mg. of choline chloride given intravenously accelerates the movements of the stomach and small intestine. G. B.

Liver Function. Benzoate Administration and Hippuric Acid Synthesis. G. D. DELPRAT and G. H. WHIPPLE (*J. Biol. Chem.*, 1921, 49, 229–246).—A severe liver injury, for instance, extensive necrosis due to chloroform, delays but does not prevent the synthesis of hippuric acid. The authors attribute the synthesis in these cases to the subsidiary action of other cells of the body. The intravenous administration of benzoate always increases ammonia, urea, and total nitrogen of the urine. Under certain conditions benzoate injection causes a considerable breakdown of protein, due probably to the acute need of glycine. G. B.

The Part Played by Acid in Carbohydrate Metabolism. IV. The Relation between Acid and Alkali and Adrenaline-glycosuria. H. ELIAS and U. SAMMARTINO (*Biochem. Z.*, 1921, 117, 10–40; cf. A., 1919, i, 54).—Glycosuria induced by injection of acids into rabbits does not cause congestion of the liver such as occurs in piqure or adrenaline glycosuria. There is marked acidosis produced in rabbits by subcutaneous administration of adrenaline, the lactic acid content of the liver increasing threefold. The mobilisation of sugar produced by adrenaline in isolated tortoise liver is inhibited by alkali, but restored by neutralisation. H. K.

Energy Exchanges in Muscle. IV. Formation of Lactic Acid in Cut Muscle. OTTO MEYERHOF (*Pflüger's Archiv*, 1921, 188, 114–160; from *Chem. Zentr.*, 1921, iii, 892; cf. A., 1921, i, 76).—In the estimation of lactic acid in frog's muscle, the material is extracted directly with 96% ethyl alcohol. The extract is evaporated to dryness, and the residue ground and washed with saturated sodium sulphate solution. The lactic acid maximum observed in cut muscle is attributed to inhibition of its production owing to increase of acidity. By varying the conditions, the whole of the glycogen may be changed into lactic acid. Addition of dextrose, hexosephosphoric acid, or glycogen to muscle suspended in a phosphate solution does not increase the rate of formation of lactic acid if the addition takes place in the first hour. Disappearance of lactic acid runs parallel with oxidation. Whilst under anaerobic conditions there is an equivalence between the disappearance of carbohydrate and the formation of lactic acid, the equivalence of the reverse process does not hold for cut muscle.

A correlation exists between respiration intensity and lactic acid formation. In cut muscle, respiration intensity is nearly equal to the maximal respiration intensity for uncut muscle. G. W. R.

The Oxidative Degradation of Dextrose in the Animal Body. JULIUS HIRSCH (*Biochem. Z.*, 1921, **117**, 113—116).—By use of dimethylhydroresorcinol (dimedon) as a fixative for acetaldehyde, the presence of acetaldehyde in 900 grams of frog's muscle was detected by isolation of 0.3 gram of condensation product (aldomedon). H. K.

Fixation of Lime by Animal Tissues. III. E. FREUDENBERG and P. GYÖRGY (*Biochem. Z.*, 1921, **118**, 50—54; cf. A., 1921, i, 382).—Cartilage which has absorbed the alkaline-earth metals has also the power of fixing phosphate. The colloids of the cartilage are assumed to play a part in this chemical combination. H. K.

Zinc in the Human and Animal Organism. E. ROST (*Med. Klin.*, 1921, **17**, 123—124).—In the human body zinc is to be found in almost all organs and tissues, particularly in the liver and in the muscles. In the liver of infants there is 39—82 mg. per kilo. of tissue, in adults, 52—145 mg. per kilo. Zinc is present in the secretions (milk, urine, faeces), and in epidermal structures such as hair. Human milk contains 1.3—1.4 mg. per litre; goat milk 2.3 mg.; cow milk 3.9 mg. In the urine 0.6—1.6 mg., and in the faeces 3—19 mg. are eliminated daily. Hair contains 9 mg. per kilo. The zinc is derived largely from the meat eaten but some is taken in as vegetable matter. In the tissues, the zinc exists in a more or less firm union with protein. (CHEMICAL ABSTRACTS.)

The Measurement of the Influence of Heat and Light on the Activity of Reduction of Animal Tissues, and Applications to Heliotherapy. J. VALLOT (*Compt. rend.*, 1921, **173**, 1196—1198).—The rate of reduction of methylene-blue by animal tissues is markedly increased by rise in temperature or by an increase in the intensity of the illumination and the beneficial therapeutic effects of solar radiation are attributed to this increased activity of reduction. W. G.

The Chemical Composition of Starfish. GUSTAV HINARD and ROBERT FILON (*Compt. rend.*, 1921, **173**, 935—937).—The oil extracted from fresh starfish has d_{25}^{25} 0.9372; $n_D^{22} + 47^\circ$ (Amagat and Jean); brismer index 48° ; iodine value (Wijs) 132.7; saponification value 159.1; unsaponifiable matter 38.94%. W. G.

Inorganic Constituents of Milk. I. Chlorides in Human Milk. W. R. Sisson and W. DENIS (*Amer. J. Dis. Children*, 1921, **21**, 389).—The average chloride content of all specimens examined was 58.2 mg. Cl per 100 c.c. It is higher in the first weeks of lactation, and after the second week the average is 52.6 mg. Cl per 100 c.c. G. B.

The "Alkaline Tide" after Meals. I. CYRUS H. FISKE (*J. Biol. Chem.*, 1921, 49, 163—170).—The author lays stress on the P_H of the urine, rather than on titration values. The influence of the food taken renders the interpretation of small variations of P_H uncertain, but after a full meal an undoubted increase in alkalinity occurs quite suddenly in the second or third hour. G. B.

Inorganic Phosphate and Acid Excretion in the Post-absorptive Period. CYRUS H. FISKE (*J. Biol. Chem.*, 1921, 49, 171—181).—During the night the rate of excretion of inorganic phosphorus in the urine is greater ($1\frac{1}{2}$ times to twice) than during the day. This the author attributes to retention of phosphorus in the morning. The rate of phosphate excretion is to some extent parallel to the hydrogen-ion concentration, but does not wholly account for the variations in the latter (cf. preceding abstract). G. B.

The Iodine Number of Urine. OSKAR WELTMANN (*Wiener Arch. inn. Med.*, 1921, 2, 107—120).—The affinity of urines for iodine normally varies directly with the density and inversely with the amount of the urine. The amount of iodine with which 100 c.c. of urine combines is termed the "percentage iodine number," and the corresponding amount for twenty-four hours, the "absolute iodine number." When the iodine number and the density show wide variation, a relatively high iodine number indicates extra-renal factors, and a relatively low iodine number, a severe injury to the kidney. High iodine numbers have been noted in certain diseases of the liver, acute febrile conditions, and certain rapidly progressing malignant neoplasms.

CHEMICAL ABSTRACTS.

Amino-nitrogen in the Urine by the Formol Method. C. CIACCIO (*Arch. Sci. med.*, 1920, 43, 177—181).—This nitrogen is considered to be present not as amino-acids, but as polypeptides. This conclusion is based on a comparison of results by the Henriquez method and those obtained by a preliminary treatment with mercuric acetate, or by tannin and lead acetate. G. B.

Quantitative Measurement of the Transient Excretion of Caffeine in Man by a New Biological Method. EDUARD FRIEDBERG (*Biochem. Z.*, 1921, 118, 164—184).—The method depends on the observation that there is a sharp contraction of the transversely striped musculature of the frog at a concentration of caffeine of 1 in 3,500. The caffeine in urine is isolated from the dried residue by extraction with chloroform. In man, diuresis is not solely dependent on the dose of caffeine, but partly on the water content of the tissues. The cessation of excretion of caffeine is early, possibly due to degradation of the caffeine to a methyl-xanthine. The smallest proportion of caffeine taken by the mouth and recognisable in the urine is 10 mg. H. K.

A Red Colouring Matter Produced by the Action of *p*-Dimethylaminobenzaldehyde on Normal Urine. PAUL HÁRI (*Biochem. Z.*, 1921, 117, 41—54).—When *p*-dimethylamino-

benzaldehyde is added to a hot concentrated urine which has previously been treated with lead acetate, a dark red coloration is produced. On cooling, and careful addition of ammonia, the colouring matter is precipitated and may be purified by crystallization from dilute alcohol. Ten to 12 litres of fresh urine yield 0.02 to 0.06 gram of pure substance, m. p. about 220°. The spectral behaviour of the substance has been examined and its extinction coefficient used as a measure of purity. Its tinctorial power is very great. The substance is apparently not identical with the colouring matter of Ehrlich's reaction on pathological urine.

H. K.

Origin and Destiny of Cholesterol in the Animal Organism.

XII. The Excretion of Sterols in Man. JOHN ADDYMAN GARDNER and FRANCIS WILLIAM FOX (*Proc. Roy. Soc.*, 1921, [B], 92, 358—367).—The present paper revises earlier results (Ellis and Gardner, A., 1913, i, 222). It is now shown that, in man, the amount of sterols excreted in the faeces is in excess of that taken in with the food. The intake, however, of unsaponifiable matter not precipitated by digitonin (cf. A., 1921, i, 639) is larger than the output. It is concluded from the results that the human organism is capable of synthesising cholesterol.

E. S.

Experimental Toxic Hæmatoporphyria. PIETRO BINDA (*Arch. Farm. speriment. Sci. aff.*, 1921, 31, 184—191).—The results of the author's experiments with rabbits indicate that chronic sulphonal poisoning does not determine elimination of hæmatoporphyrin by the kidneys, that animals poisoned by sulphonal keep their power of retaining and elaborating injected hæmatoporphyrin, and that in the organs of animals killed by chronic sulphonal poisoning, the original property of reducing hæmatoporphyrin *in vitro* is preserved.

T. H. P.

Blood Fat in Diabetes. N. R. BLATHERWICK (*J. Biol. Chem.*, 1921, 49, 193—199).—Cases of mild and moderate diabetes can utilise satisfactorily large amounts of fat as indicated by the blood fat level and the absence of acetone substances from the urine.

G. B.

Lipæmia. W. R. BLOOR (*J. Biol. Chem.*, 1921, 49, 201—227).—In most cases a sequence in the appearance and disappearance of fat, lecithin, and cholesterol is perceptible, fat being the first to increase and to disappear. In most cases the ratio lecithin/cholesterol is distinctly below normal, as the cholesterol is increased in greater proportion than the lecithin. The increase in fat is generally in still greater proportion.

G. B.

Action of certain Bismuth Derivatives on Syphilis.

R. SAZERAC and C. LEVADITI (*Compt. rend.*, 1921, 173, 1201—1204).—It is shown that ammoniacal bismuth citrate, bismuth lactate, bismuth subgallate, and bismuth oxyiodogallate are all active against syphilis, but vary in their toxic power. For human

therapeutics sodium or potassium bismuthotartrate are the best bismuth preparations to use. W. G.

The Action of Polished Metals on Toxins. F. ERDSTEIN and L. FÜRTH (*Biochem. Z.*, 1921, **118**, 256—258).—A confirmation of Luger and Baumgarten's results (*Wien. klin. Woch.*, 1912, 1222) that copper and to a very slight extent silver have a harmful effect on toxins. An actual destruction of the toxin takes place in the sense that a complex metal-toxin compound is formed. H. K.

Toxicity of Methyl Alcohol. ASTRID CLEVE VON EULER (*Svensk. Kem. Tidskr.*, 1921, **33**, 114—119; from *Chem. Zentr.*, 1921, iii, 740).—Methyl alcohol is considered by the author to be less poisonous in large doses than ethyl alcohol. Cases of poisoning by methyl alcohol are to be attributed to accompanying poisonous impurities. G. W. R.

The Action of Organic Kations on the Vascular System and its Modification by Inorganic Ions. WERNER TESCHENDORF (*Biochem. Z.*, 1921, **118**, 267—285).—The action of a number of salts of strong organic bases was examined on the frog's vascular system. Acetylcholine had the most powerful constricting action. Nitrosocholine was much less active and guanidine still less so. In the homologous series of quaternary ammonium bases, tetramethylammonium chloride was intermediate between acetylcholine and nitrosocholine, the tetraethyl derivative resembled guanidine, whilst the tetrapropyl derivative depressed the vascular tonus. The action of the above organic kations was inhibited by the bivalent inorganic kations in the order: Mg, Ca, Sr, Ba. H. K.

Degradation of Fatty Acids in the Animal Organism. P. WORINGER (*Bull. Soc. Chim. Biol.*, 1921, **3**, 311—450).—A review on much the same lines as Dakin's monograph. Here and there the author puts forward independent views. Thus he argues against Dakin's conception of the breakdown of tyrosine and phenylalanine, and considers that the fundamental condition necessary for the combustion of an aromatic substance is its capacity of being transformed into homogentisic acid. He thus accepts Abderhalden's view (*A.*, 1912, ii, 585) that this acid is produced in the normal tyrosine metabolism.

The title of the review scarcely represents its full scope, as it also deals with hydroxy-, keto-, and amino-acids. A special feature is a tabulation of the transformations of acids hitherto observed in the animal, with a statement of the method employed and a literature reference. There is also a full bibliography.

G. B.

A New Antianaphylactic Substance, Sodium Formaldehydesulphoxylate. P. BRODIN and P. HUCHET (*Compt. rend.*, 1921, **173**, 865—867; cf. *ibid.*, 1919, **168**, 369; **169**, 9).—Sodium formaldehydesulphoxylate, $\text{CH}_2(\text{OH})\text{SO}_2\text{Na}$, can be injected into dogs or rabbits to the extent of 1 gram per kilo. of live weight without any ill-effect and, like sodium chloride, it has an immunising action against an anaphylactic injection.

W. G.

The Behaviour of Pyrrole in the Animal Body. TOMIHIDE SHIMIZU (*Biochem. Z.*, 1921, 117, 266—268).—Injection of an aqueous suspension of pyrrole into dogs is followed by its elimination in the urine as methylpyridine. H. K.

Behaviour of Phrenosine in the Animal Body. TOMIHIDE SHIMIZU (*Biochem. Z.*, 1921, 117, 263—265).—Phrenosine administered to a dog appeared in the urine as sphingosine; the latter, when given either by the mouth or subcutaneously, to dogs or rabbits, appeared unchanged. H. K.

Chemistry of Vegetable Physiology and Agriculture.

The Nature of the Butyric Acid and Butyl Alcohol Fermentation. Fixation of Acetaldehyde as a Decomposition Product. Transformation of the Aldol of Pyruvic Acid into Butyric Acid. Production of Higher Fatty Acids from Sugar. CARL NEUBERG and BERNHARD ARNSTEIN (*Biochem. Z.*, 1921, 117, 269—314).—Dextrose in a nutrient medium of inorganic materials and in the presence of a fixative, for example, sodium sulphite, is fermented by *Bacillus butylicus*, Fitz, with production of about 10% of acetaldehyde. By the use of a culture of *Amylobacter*, acetaldehyde could also be qualitatively recognised. Acetaldehyde or its condensation product, aldol, is not the intermediate stage in the butyric fermentation, but the aldol of pyruvic acid, α -keto- γ -valerolactone- γ -carboxylic acid, which gave butyric acid on fermentation. Starch syrup fermented by a culture of *B. butylicus*, Fitz, in an inorganic nutrient medium gave small quantities of the higher fatty acids of which decolic was identified. H. K.

Action of *Aspergillus glaucus* on Glycerol. F. TRAETTA-MOSCA and M. PRETI (*Gazzetta*, 1921, 51, ii, 269—277).—When *Aspergillus glaucus* is grown in a nutrient liquid containing glycerol, the latter yields the compound, $C_6H_6O_4$, m. p. 154°, previously obtained from sucrose or invert-sugar by the action of the same mould (A., 1914, i, 1114). This compound forms a *methyl ether*, $C_6H_5O_3OMe$, which crystallises in white needles, m. p. 165°, and, unlike the original compound, gives no coloration with ferric chloride solution. Hydrolysis of the methyl ether by means of barium or calcium hydroxide results in the formation of methyl-acetol ether and oxalic and formic acids, whilst the action of ammonia yields pyridone. The structure of the compound, $C_6H_6O_4$, is probably $CH \begin{smallmatrix} \diagup CH-CO \\ \diagdown O-C(OH) \end{smallmatrix} > C \cdot CH_2 \cdot OH$, and is similar to Peratoner and Tamburello's maltol (A., 1905, i, 807). T. H. P.

The Longevity of certain Species of Yeast. ARTHUR R. LING and DINSHAW RATTONJI NANJI (*Proc. Roy. Soc.*, 1921, [B], 92, 355—357).—Cultures of eight different species of yeast were found to be still alive after thirty-four years' storage on dry cotton wool pads contained in sealed flasks. E. S.

Alcoholic Fermentation by means of Yeast-cells under Various Conditions. I. Influence of Animal Charcoal and other Adsorbents on the Course of the Fermentation: Formation of Acetaldehyde. EMIL ABDERHALDEN (*Fermentforsch.*, 1921, 5, 89—109).—The addition of animal charcoal to a solution containing sugar and yeast-cells effects acceleration of the fermentation, and such acceleration appears to be due to the formation of acetaldehyde, which is always detectable in the liquid under these conditions. It is uncertain if the acetaldehyde is a product of the degradation of the dextrose or a secondary product formed by oxidation of the ethyl alcohol, but it is found that addition of yeast and animal charcoal to aqueous alcohol results, after a time, in the appearance of an odour of acetaldehyde.

Since animal charcoal is an excellent adsorbent for acetaldehyde, it is possible, not only that it takes part in the secondary formation of acetaldehyde from ethyl alcohol, but that it concentrates on its surface and thus renders detectable acetaldehyde formed as a primary product of the fermentation of sugar. T. H. P.

Alcoholic Fermentation by means of Yeast-cells under Various Conditions. II. EMIL ABDERHALDEN (*Fermentforsch.*, 1921, 5, 110—118; cf. preceding abstract).—Further investigations show that acetaldehyde solutions which show no loss in weight when left in contact with either animal charcoal or yeast, immediately begin to evolve gas when both the charcoal and yeast are added. Experiments were made also with pyruvic acid and with methyl and ethyl alcohols, it being found that all the samples of animal charcoal tried accelerated the fermentation of sugar by means of yeast, caused formation of acetaldehyde, and induced formation of acetaldehyde and carbon dioxide from pyruvic acid, but that some samples were totally unable to effect transformation of acetaldehyde or alcohols. T. H. P.

Functions of the Yeast-cell. Zymase and Carboxylase Action. EMIL ABDERHALDEN and A. FODOR (*Fermentforsch.*, 1921, 5, 138—163).—The authors consider that the fermentations effected by zymase in its plasma form and by liberated zymase are, quantitatively and kinetically, different processes and have carried out various experiments with the object of ascertaining how dried yeast differs from the living cell and what substances are removed from living or dried yeast by pressing or maceration.

Dried yeast is found to contain cells which, in a fermentable solution, swell and resume their life functions. Like yeast juice, yeast sterilised by treatment with acetone or by age is incapable of fermenting dilute sugar solutions, all such preparations lacking the ability to concentrate peculiar to the living cells. Apparently

owing to its simpler and more independent relation to the protoplasm, the carboxylase of dried yeast is able to exert its activity before the whole of the water necessary for the complete vital functions has been absorbed.

The results of various experiments with maceration juice are described, these dealing with the kinetics of the fermentation, with the persistence, both of the fermentative activity and of the carboxylase of the juice, with the oxygen absorbed by the juice, and with kinetic measurements on mixtures containing pyruvic acid, dipotassium hydrogen phosphate, and maceration juice. The fermentative ability and the power to absorb oxygen fall gradually to zero together.

T. H. P.

Vitamine Content of Rice by the Yeast Method. Organic Nitrogen as a Possible Factor in Stimulation of Yeast.

WILLIAM D. FLEMING (*J. Biol. Chem.*, 1921, **49**, 119—122).—The stimulation of yeast growth is not due to water-soluble vitamin-B, for it persists after the rice extracts have been evaporated with 10% sodium hydroxide to inactivate the vitamin. The stimulation is due to organic nitrogen (cf. Fulmer, Nelson, and Sherwood, *A.*, 1921, i, 292).

G. B.

Comparative Experiments on the Inhibitive Action of some Chlorine Derivatives of Methane, Ethane, and Ethylene on Fermentation. H. PLAGGE (*Biochem. Zeitsch.*, 1921, **118**, 29—143).— $\alpha\alpha$ -Dichloro- and $\alpha\beta$ -dichloro-ethane, dichloromethane, chloroform, and tetrachloroethane are toxic to the yeast-cell. The determining factor is not the concentration of the solution, but the actual dose administered.

H. K.

Fermentation without Yeast. EMIL BAUR and EUGEN FERZFELD (*Biochem. Z.*, 1921, **117**, 96—112).—Mixtures of substances in imitation of yeast press juice (peptone, dextrose, dextrin, sodium hydrogen carbonate, casein, lipoid, and bile salts) produced carbon dioxide and alcohol (iodoform test) in small amounts. The formation of acid substances from dextrose, liberating carbon dioxide from the sodium hydrogen carbonate, only accounts for a portion of the gas formed.

H. K.

Behaviour of Diastase and other Enzymes under Unfavourable Conditions. Action of some Nitrogenous Compounds on Germination. TH. BOKORNY (*Bied. Zentr.*, 1921, **50**, 429—430).—Brief reference is made to the effect of acids, bases, salts of heavy metals, etc., on such enzymes as diastase, invertase, pepsin, myrosin, and trypsin.

From an examination of the effect of urea, hippuric acid, ammonium salts, and sodium nitrate on germination, it is shown that nutrient materials are injurious if used at too high a concentration.

W. G.

The Manganese Content of (Dutch) Seeds. D. H. WESTER (*Biochem. Z.*, 1921, **118**, 158—163).—The manganese content of the seeds of 48 species of plants was determined, the quantity of

metal generally present being between 2 and 6 mg. in 100 grams of dried material. H. K.

Is it Possible to Determine the Value of Seeds by a Biochemical Method? ANTOINE NÈMEC and FRANÇOIS DUCHOÏN (*Compt. rend.*, 1921, 173, 933—935).—The activity of the various hydrolysing enzymes such as amylase, invertase, glycerophosphatase, lipase, urease, uricase, and phytoproteases of seeds diminishes with the germination capacity of the seeds, but is still marked when the latter has reached zero. Catalase is different, and there is some indication that the activity of the catalase, measured under comparable conditions, may represent a suitable means for determining rapidly and simply the agricultural value of seeds. W. G.

Corrosive Action of Roots on Marble. E. CHEMIN (*Compt. rend.*, 1921, 173, 1014—1016).—Further experiments are given in support of the view that plant roots do not excrete any sensible amount of acids other than carbonic acid and that the excretion of the latter is sufficient to explain the corrosion of marble. W. G.

The Part Played by Lipoids in the Metabolism of Plant Cells. FRIEDRICH BOAS (*Biochem. Z.*, 1921, 117, 166—214).—The influence of saponin and salts was investigated on the growth of yeast and the course of fermentation. The action of these agents is similar to their known action on animal cells, the combined action leading to destruction of the cell. The anions and kations of the salts influence the colloidal state of the cell wall and follow the lyotrope series. H. K.

The Effect of Neutral Salts on the Heat Coagulation of Plant Protoplasm. HUGO KAHHO (*Biochem. Z.*, 1921, 117, 87—95).—Both ions of neutral salts play a part in the heat coagulation of the protoplasm of the epidermal cells of *Tradescantia zebrina*. The coagulation is accelerated by anions arranged in the lyotropic series. Neutral salts which penetrate the plasma membranes most readily have the greatest lowering effect on the temperature of coagulation. H. K.

The Relation between Fluorescent Substances which Act in the Dark and their Photodynamic Activity on Cells. A. JODLEAUER and F. HAFNER (*Biochem. Z.*, 1921, 118, 150—157).—A large number of fluorescent and non-fluorescent substances of known photodynamic action on cells (for example, paramoecia) have been examined in respect of their action in the dark, on the hæmolysis of erythrocytes at room temperature and at 56°, and in the flocculating property on the colloidal contents of hæmolysed corpuscles at 56°. In general there is a parallelism between the two actions. H. K.

Rhythmic Precipitation Phenomena in Cell Membranes of Plants. HANS PETER MÜLLER (*Kolloid Chem. Beihefte*, 1921, 14, 97—146).—When wheat grains which have been cut are treated with a solution of silver nitrate, bands and layers are formed at

right angles to the direction of diffusion in the membranes of the aleurone cells and in the nucellus layer, which are identical with the zones discovered by Liesegang in artificial colloids. The identity between the rhythmic precipitation in plant cells and Liesegang's rings and zones is proved, (1) by the form and appearance of the bands and (2) by the fact that the effect of external agencies is the same in both cases. In both cases, the rhythmic precipitation of silver nitrate occurs after a region of formless precipitate; zones are produced which increase in width and distance apart with increasing distance from the centre of diffusion. With increasing width, the formation of grains occurs and the edges of the zones become indistinct, the space between the zones becomes turbid, and finally the rhythmic zone formation passes over into an irregular granular precipitate. Fick's law of diffusion is approximately applicable to the diffusion of silver nitrate in wheat grains, the water content of the membrane, its content on silver nitrate, and the concentration of silver nitrate have the same influence as in the diffusion into jellies. The formation of a rhythmic precipitation depends on the velocity of diffusion of silver nitrate. The zone formation commences so much nearer to the centre of diffusion the smaller the concentration of silver nitrate and the lower the temperature. The velocity of invasion of the silver is of equal importance, which apart from the concentration of silver nitrate is influenced by the content of the cell walls on silver precipitating salts and water. In wheat grains a larger and smaller rhythm cannot be detected. The dimensions of the width and distance between the bands are the same for plant cells which have had a previous treatment with silver nitrate and those which have not been so treated. The grains of other cereals, and the leaves of many plants show a similar zone formation when treated with silver nitrate, so that it may be assumed that the cellulose membranes of plants in general are capable of showing rhythmic precipitation when the necessary external conditions are obtained. From the experiments it follows that the pure cellulose membranes of the wheat grain which show rhythmic precipitation cannot be regarded as a selective permeable layer, and it further follows that the woody integument layer of the sheath of the wheat grain is the selective permeable membrane.

J. F. S.

The Distribution of Manganese in the Organism of Higher Plants. GABRIEL BERTRAND and (MME) M. ROSENBLATT (*Compt. rend.*, 1921, **173**, 1118--1120).—From a study of the distribution of manganese in the different parts of a dicotyledon, *Nicotiana rustica* L., and of a monocotyledon, *Lilium lanceifolium rubrum*, it is shown that those organs in which chemical changes are the most intense contain the highest percentages of manganese. The seeds contain a high proportion of manganese, doubtless for the use of the future seedling.

W. G.

Lumbang Oil (Candlenut Oil). AUGUSTUS P. WEST and ZOILA MONTES (*Philippine J. Sci.*, 1921, **18**, 619--636).—The oil is obtained from the nuts of *Alcurites moluccana* and has the following

composition: glyceryl linolenate 6.5%, glyceryl linolate 33.4%, glyceryl oleate 56.9%, glycerides of solid acids 2.8%. It is insoluble in cold ethyl and methyl alcohols and acetic acid. The oil behaves in much the same manner as linseed oil on oxidation. It is an excellent drying oil.

H. C. R.

The Odorous Constituents of Apples. F. B. POWER and V. K. CHESNUT (*J. Amer. Chem. Soc.*, 1921, 43, 1741; cf. A., 1920, i, 653).—Inasmuch as esters derived from leucic acid do not occur in apples (*loc. cit.*), the title of a paper by Kodama on this subject (cf. A., 1921, i, 220) is misleading.

W. G.

Characteristics and Utilisation of Beech Nut Oil. H. B. (*Mat. grasses*, 1921, 13, 5860—5861).—The oil content of beech nuts varies from 14 to 22%. The constants of the oil are: d_{4}^{25} 0.9205, iodine number 104.4, bromine number 0.652, heat developed with sulphuric acid +65°, polariscope reading -0.8° in saccharimeter degrees, refractometer reading +16.5 to +18°. The oil is edible and may be kept without change for a long time. The cake from the nuts gave the following analysis: decorticated cake: water 12.5%, oil 7.5%, nitrogenous matter 37.1%, non-nitrogenous extract 29.7%, cellulose 5.5%, ash 7.7%; non-decorticated cake: water 19.1%, oil 8.34%, nitrogenous matter 18.15%, non-nitrogenous extract 28.39%, cellulose 20.89%, ash 5.13%. The non-decorticated cake is poisonous.

CHEMICAL ABSTRACTS.

The Biology of the Alkaloids of Belladonna. JEAN RIPERT (*Compt. rend.*, 1921, 173, 928—930).—Belladonna plants grown in obscurity show an increase in alkaloid content both in the leaves and in the stems, whilst the amount in the roots diminishes very slightly. When the plants are returned to sunlight the values for the leaves return to a practically normal figure after thirteen days. The protein content of the leaves also increases considerably when the plants are kept in the dark.

W. G.

Anthocyanin of *Beta vulgaris*. F. M. ANDREWS (*Proc. Ind. Acad. Sci.*, 1917, 167).—The anthocyanin of *B. vulgaris* affords one of the examples where the pigment forms in the subterranean parts. A strong solution of such anthocyanin will preserve its normal colour in a test-tube placed in darkness for more than a week. In direct sunlight, it will retain its normal bright colour for a week or more, until disorganised by bacterial action, which change finally occurs in the anthocyanin solution in the dark.

CHEMICAL ABSTRACTS.

Formation of the Red Pigment of *Beta vulgaris* by Oxidation of the Chromogens. ANTOINE KOZŁOWSKI (*Compt. rend.*, 1921, 173, 855—857).—Details are given for the extraction of the chromogens from beetroot by alcohol and for their subsequent purification and isolation. The chromogens extracted from the white sugar-beet resemble saponins in certain of their physico-chemical properties and on oxidation give a coloured pigment

having the same spectroscopic characteristics as the red pigment extracted from red beetroots and showing similar colour changes with acids and alkalis. W. G.

Transformation, by Oxidation, of the Chromogens of some Plants into a Red Pigment. ST. JONESCO (*Compt. rend.*, 1921, 173, 1006—1009).—The yellow chromogens extracted from such plants as *Cobæa scandens* and *Ampelopsis hederacea* on oxidation in amyl alcoholic solution with sulphuric acid and manganese dioxide at 50—60° give a violet-red pigment. In the case of the chromogens from *Ampelopsis* reduction was tried but red pigments were not obtained. The results obtained confirm those of Kozłowski on beetroot pigments (preceding abstract) that the appearance of red pigments in plants is due to oxidation and not to reduction phenomena. W. G.

Formation of Anthocyanin in the Flowers of *Cobæa scandens* at the Expense of Pre-existing Glucosides. ST. JONESCO (*Compt. rend.*, 1921, 173, 850—852).—Contrary to the results of Rosé (A., 1914, i, 639) experimental evidence is given to show that the anthocyanin glucosides in the flowers of *Cobæa scandens* are formed at the expense of pre-existing glucosides, and consequently Combes's hypothesis as to the formation of anthocyanin (cf. A., 1909, ii, 426) is incorrect. W. G.

The Effect of Daylight on the Content of Active Material in *Digitalis*. OTTO VON DAFERT (*Bied. Zentr.*, 1921, 50, 422—425).—The toxicity of the extract from *Digitalis* leaves depends on the time of day at which the leaves are gathered and how and when the leaves are killed. To obtain the most toxic extract the leaves should be gathered in the afternoon and immediately killed by plunging them into 96% alcohol. W. G.

The Occurrence of Methyl Anthranilate in Grape Juice. FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1921, 43, 1741—1742).—Methyl anthranilate is a natural and apparently constant constituent of grape juice. Its presence, therefore, in a commercial grape juice must not necessarily be taken as an indication of adulteration. W. G.

Grape Oil from the Canadian Vine (*Vitis hederacea*). (*Boll. assoc. ital. piante med. aromat.* 2, 56—59; *Bull. Agr. Intelligence*, 1919, 10, 1004—1005).—Two oils were extracted, (1) from the pips, a dark yellow or green oil with sweet taste and nutty odour, d_{4}^{25} 0.9215, n_D^{25} 1.4778, saponification number 189.2—189.6, iodine number 131.4—141.6, fixed fatty acids 93.97%, volatile fatty acids 0%, and non-saponifiable substances 1.44%. The total fatty acids have iodine number 144.6 and mean molecular weight 281.2. Solid fatty acids consisting chiefly of palmitic acid do not exceed 3%, have a mean molecular weight of 261.4 and m. p. 57.6°. The liquid fatty acids are chiefly oleic and linoleic acids, with iodine number 148.8—149.9; (2) from the pulp and skin, an olive-green, soft, sticky oil with astringent taste and pleasant odour, turning rancid in the air, n_D^{25} 1.4722, saponification number 192.3—193.3, iodine

number 90.3, fixed fatty acids 94%, volatile fatty acids 0%, and unsaponifiable substances 1.67%. The total fatty acids have iodine number 94.4—94.6 and mean molecular weight 278.8. The solid fatty acids are about 10% of the pulp and skin oil, chiefly palmitic acid. The liquid fatty acids are mostly oleic and linoleic acids with iodine number 110.2.

CHEMICAL ABSTRACTS.

Oil from the Seeds of *Jatropha Curcas*, L. CLEMENS GRIMME (*Seifenfabr.*, 1921, **41**, 513—515; from *Chem. Zentr.*, 1921, iii, 1035).—The seeds of *Jatropha Curcas*, L., consist of 38% hard husk and 62% oil-bearing kernel. Analyses of the seeds are given. In spite of the high protein content, 48.13%, the seeds are unsuitable for use as a feeding stuff on account of the presence of highly poisonous *curcine*. A complete description is given, with constants, of the oil obtained by extraction, hot pressure, and cold pressure respectively. The principal constants are d_{4}^{25} 0.9213—0.9228; m. p. 5—8°; n_D^{20} 1.4610—1.4618; acid number 3.18—4.05; iodine number (Wijs) 96.7—98.8. The fatty acids are white to yellow in colour and have m. p. 15—18°. The oil belongs to the class of non-drying oils and consists of the glycerides of palmitic, myristic, and *curcanolic* acids. The latter is a hydroxy-acid like ricinolic acid. The seeds contain a lipolytic enzyme which, however, is not so energetic as the enzyme in *Ricinus* seeds.

G. W. R.

Iodine in the *Laminaria*. P. FREUNDLER, (MLLE) Y. MENAGER, and (MLLE) Y. LAURENT (*Compt. rend.*, 1921, **173**, 931—932).—An examination of the iodine content of certain species of *Laminaria* shows that they lose a certain amount of iodine during drying, the loss amounting in some cases to as much as 50%. The iodine content is dependent on the time of harvesting, being higher in July than in March. It is independent of the place of growth, but varies with the age of the tissues, being highest in the youngest tissues. The variations with different parts of the plant are not uniform, but differ with the species.

W. G.

The Composition of the *Laminaria*. P. FREUNDLER, (MLLE) Y. MENAGER, and (MLLE) Y. LAURENT (*Compt. rend.*, 1921, **173**, 1116—1118; cf. preceding abstract).—The authors have correlated the variation in iodine content of the *Laminaria* with their biological evolution and show that the maxima for iodine content as well as for the percentages of reserve carbohydrates and brown pigments coincide with the period of maximum sunshine. The *Laminaria* regularly restore to the sea a certain amount of their iodine under conditions which depend, for each species, on their mode of growth.

W. G.

Properties and Composition of Tohaku Oil. YOSHITORA IWAMOTO (*J. Chem. Ind. Japan*, 1921, **24**, 1143—1160).—A yellowish-brown oil is obtained by pressure or extraction of the seed of "Tohaku," *Lindera obtusiloba*, B. L., which is widely diffused in Corea. Its physical and chemical constants were determined. Decoic, lauric, and oleic acids and an acid, $C_{12}H_{22}O_2$, which occurs

in cochineal fat, were identified. Some of the lower unsaturated liquid, and solid fatty, acids seem to be present, but linolic, linolenic, stearic, and palmitic acids are probably absent. K. K.

The Proteins of the Alfalfa Plant [Lucerne]. THOMAS B. OSBORNE, ALFRED J. WAKEMAN, and CHARLES S. LEAVENWORTH (*J. Biol. Chem.*, 1921, **49**, 63—91).—The paper is mainly concerned with a technique for extracting plant proteins with as little change as possible. Fresh plants, or plants frozen soon after cutting, are ground very finely and pressed in a hydraulic press; the undiluted juice contains 10% of solids. The addition of 20% of alcohol precipitates a colloid, consisting of 70% of protein and calcium salts. The latter are extracted by dilute alcoholic hydrochloric acid, which forms an insoluble hydrochloride of the protein. The latter is further purified by heating with dilute alkali hydroxide, and reprecipitation. By successive extraction with water, alcohol, dilute aqueous alkali, and hot alkaline alcohol, practically all the cell contents can be extracted if the fresh plant is sufficiently thoroughly ground. Thirty-two per cent. of the solids of the plant, containing only 5.6% of its nitrogen, finally remains undissolved. G. B.

The Odorous Constituents of Peaches. FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1921, **43**, 1725—1739).—An examination of the pulp of choice, ripe peaches shows that the odorous constituents of the fruit consist chiefly of the linalyl esters of formic, acetic, valeric, and octoic acids, together with a considerable proportion of acetaldehyde and a very small amount of an aldehyde of higher molecular weight. It is probable that the volatile acids are present to some extent in a free state. No trace of hydrocyanic acid or benzaldehyde could be detected in the distillate from peach pulp. The yield of essential oil was about 0.00074% of the fresh pulp, and the oil contained, in addition to the linalyl esters, a little acetaldehyde and furfuraldehyde, probably some cadinene and a very small amount of an unidentified paraffin hydrocarbon. The essential oil is very unstable and on exposure to air for any length of time is converted into a black, viscid mass and loses its original fragrance.

The emanation from the entire ripe fruit contains a minute amount of acetaldehyde. W. G.

Constituents of *Phellodendron Amurense*. KŪTARŌ SHIMO (*Sci. Rep. Tohoku Imp. Univ.*, 1921, **10**, 331—338).—The rind of *Phellodendron Amurense* contains berberine and fatty acids. These acids appear to exist uncombined with berberine and consist of palmitic acid, linoleic acid, and a small quantity of linolenic acid. A small quantity of a neutral substance was found in addition but was not identified. Two samples of phellodendron rind gave 2.473% and 3.75% respectively of berberine (estimated as berberine acetone). G. W. R.

The Cellulose Content of Pine Wood. PETER KLASON (*Zellstoffchem. Abhandlungen*, 1921, **1**, No. 6, 105—114).—Cross and Beman's method cannot be used for the estimation of the cellulose

content of pine wood. The author has investigated the action of a solution of 80 grams of sodium hydrogen sulphite and 500 c.c. of *N*-hydrochloric acid in one litre of water for varying periods of time at 100°. After eight days the cellulose reaches a nearly constant value, and, with continued heating, only slowly decreases (1.7% in 13 days). He finds 53% of cellulose in pine wood. The composition of woods of various ages is also investigated.

CHEMICAL ABSTRACTS.

Chemical Constituents of Pine Leaves. II. ASTRID CLEVE VON EULER (*Tekn. Tidsk. Kem. Berg.*, 1921, 51, 35—38, 47—52).—A study of the non-fatty impurities, insoluble in ethyl ether, present in the crude fat of pine leaves. The material is more conveniently extracted by means of 93% methyl alcohol, and is designated "crude gum." It readily changes into an insoluble substance, the change being facilitated by the presence of acids. A solution of the gum in sodium hydroxide showed marked changes when treated with carbon dioxide. Fractional precipitation of the alkaline solution of the gum with acids yielded coniferyl alcohol and dihydroxy- γ -phenylpropyl alcohol; the whole crude gum is tannin-like in character, and is considered to consist of intermediates in the plant synthesis of tannins. CHEMICAL ABSTRACTS.

The Organic Acids of *Pyrus coronaria*, L., *Rhus glabra*, L., and *Acer saccharum*, Marsh. CHARLES E. SANDO and H. H. BARTLETT (*J. Agric. Research*, 1921, 22, 221—229).—The organic acids of the wild American crab apple, *Pyrus coronaria*, L., smooth sumac, *Rhus glabra*, L., and sugar maple, *Acer saccharum*, Marsh, were investigated. In all cases the acid found was malic acid, occurring in the form of the free acid in the first species, the acid calcium salt in the second species and both acid and normal calcium salts in the third species. A certain amount of gallic acid is also found in the second species. The substance known as "maple sand" obtained in the preparation of sugar from the sugar maple is crude calcium malate. It appears that succinic acid may be formed autolytically from the malic acid of *Pyrus coronaria*.

G. W. R.

Volatile Substances from the Bark of *Rhamnus frangula*. O. A. OESTERLE (*Schweiz. Apoth.-Zeit.*, 1921, 59, 341—345; from *Chem. Zentr.*, 1921, iii, 734—735).—By steam distillation of the bark of *Rhamnus frangula*, 0.05—0.1% was obtained of a substance of unpleasant odour, which contained, in addition to dark coloured impurities, a white substance, insoluble in sodium carbonate, crystallising from chloroform-light petroleum in long needles, a compound obtained as a gelatinous precipitate from hot sodium hydroxide solution, a substance crystallising from hot water in slender, ray-like aggregates, and a main portion consisting of brownish-yellow platelets with a green tinge crystallising from dilute ethyl alcohol. The latter substance is tasteless and odourless, and has the empirical formula $C_{15}H_{12}O_4$. It is easily soluble in organic solvents, and has m. p. 100—101°.

G. W. R.

Organic Chemistry.

Relation between the Molecular Properties and the Capacity for Fixation of Iodine of certain Hydrocarbons. PAUL WOOD (*Compt. rend.*, 1921, 173, 1471—1473; cf. A., 1921, ii, 575).—Plotting the molecular weights of a homologous series of American oils against the corresponding iodine values reduced proportionately to the double linkings as calculated from the mean molecular surface area on water (*loc. cit.*), a regular curve was obtained, given by the equation $\log I_M + K = \log I_{M+50}$ where I_M is the iodine value for any molecular weight and I_{M+50} the value for a molecular weight fifty units higher, and K is a constant equal to 0.0664. This progressive capacity for addition or substitution is apparently due to causes analogous to those responsible for the dissociations which occur in the "cracking" process. Benzene solutions of these oils rapidly undergo oxidation when exposed to sunlight and the velocity of oxidation increases with the number of double bonds in the molecule. W. G.

A General Method for the Preparation of Carbides of Metalloids, and the Existence of Carbides of Phosphorus and Arsenic. E. DE MAHLER (*Bull. Soc. chim.*, 1921, [iv], 29, 1071—1073).—The chloro-derivative of the metalloid is allowed to react in ethereal solution at the ordinary temperature with one of Iotsch's compounds (cf. A., 1914, i, 393) of the type $\text{MgI} \cdot \text{C} \cdot \text{MgI}$, when the carbide of the metalloid is obtained. In this way, phosphorus trichloride gives phosphorus carbide, $\text{P} \begin{smallmatrix} \text{C} \cdot \text{C} \\ \diagup \quad \diagdown \\ \text{C} \cdot \text{C} \end{smallmatrix} \text{P}$, an amorphous, white compound, which is spontaneously inflammable when gently warmed, and yields phosphoric anhydride and carbon dioxide. Arsenic chloride gives arsenic carbide, As_2C_3 , a brown, amorphous compound, which explodes when warmed or gently rubbed, arsenic and carbon being liberated. W. G.

Some Aliphatic Fluorides. F. SWARTS (*Bull. Soc. chim. Belg.*, 1921, 30, (ii), 302—315).—The following are described: *n*-Amyl fluoride, a volatile, mobile liquid, m. p. below -80° , b. p. 62.8° , d_{20}^{20} 0.7960, d_4^{20} 0.7880, n_D^{20} 1.35622, n_D^{25} 1.36183, n_D^{30} 1.36533. *n*-Decyl fluoride, a mobile liquid, which solidifies in a mixture of alcohol and solid carbon dioxide, b. p. about 183.5° , d_{20}^{20} 0.792. *iso*-Amyl fluoride, b. p. 53.5° . *n*-Heptyl fluoride, m. p. -73° , b. p. $119^\circ/755$ mm., d_4^{20} 0.8029, n_D^{20} 1.38358, n_D^{25} 1.3855, n_D^{30} 1.3899, n_D^{35} 1.39358. *n*-Octyl fluoride, b. p. $142.5^\circ/75$ mm., d_4^{20} 0.81200, d_4^{25} 0.8036, n_D^{20} 1.3952, n_D^{25} 1.3970, n_D^{30} 1.40175, n_D^{35} 1.43565. Cetyl fluoride is solid at the ordinary temperature, VOL. CXXII, i. e

b. p. 287.5°/760 mm., 181°/24 mm., d_{20}^{20} 0.809. *sec.-Octyl fluoride*,
b. p. 139.3°.

It is stated that mercury fluoride is preferable to silver fluoride for the preparation of the above, several reasons being given. The yield is diminished in each case by the formation of an ethylenic hydrocarbon and hydrogen fluoride; when silver fluoride is used, this may take place in such a way that two molecules of the alkyl haloid, containing C_n , condense to yield $C_{2n}H_{4n+1}F$; sometimes this represents the major reaction. The chemical properties of the substances are described; they are, in general, not so stable as the majority of organic fluorine compounds. The *iso*alkyl fluorides tend to decompose into ethylenic hydrocarbons and hydrogen fluoride on distillation; with straight-chain compounds this is not the case. The action of alkali hydroxides in aqueous or alcoholic solution is feeble; concentrated sulphuric acid reacts in the cold with formation of hydrogen fluoride.

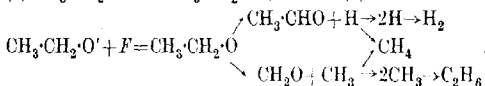
H. J. E.

The Aliphatic Sulphonamides. I. PERCIVAL WALTER CLUTTERBUCK and JULIUS BEREND COHEN (T., 1922, **121**, 120—128).

The History of [Ethyl] Alcohol. EDMUND O. VON LIPPMANN (Chem. Ztg., 1922, **46**, 4—5).—Historical.

Dehydroxidation of Alcohols. ERICH MÜLLER (Z. Elektrochem., 1921, **27**, 563—567; cf. this vol., i, 109).—A number of alcohols, including ethyl alcohol, propyl alcohol, *isobutyl* alcohol, *isopropyl* alcohol, benzyl-alcohol, ethylene glycol, glycerol, and mannitol, in strongly alkaline solution on electrolysis or in the presence of oxidising agents such as potassium ferricyanide or in the presence of colloidal rhodium, give rise to hydrogen or hydrocarbons. The reaction is explained by the assumption that in the oxidation of alcohols to aldehydes a metastable intermediate product is formed which, in the presence of metals, breaks down to hydrogen or hydrocarbons according to the scheme:

(1) $CH_3\cdot CH_2\cdot OH \rightleftharpoons CH_3\cdot CH_2\cdot O' + H'$ and (2)



J. F. S.

The Influence of Potassium Hydroxide on the Formation of Vinyl Alcohol from Acetaldehyde. WILLIAM LLOYD EVANS and CLOYD D. LOOKER (J. Amer. Chem. Soc., 1921, **43**, 1923—1928).—Poleck and Thummel's vinyl oxymercurochloride (A., 1890, 112) is obtained when alkaline solutions of acetaldehyde are treated with mercuric chloride, the yield of the oxymercurochloride being proportional to the concentration of the alkali present. Thus the production of vinyl alcohol is likewise proportional to the concentration of the alkali, and since vinyl alcohol is a necessary intermediate product in the formation of oxalic acid in the oxidation

of ethyl alcohol and acetaldehyde, the yield of oxalic acid must also be proportional to the concentration of the alkali used. A minimum concentration of about 1.40 grams of potassium hydroxide per litre is necessary for the formation of vinyl alcohol at 25°.

W. G.

Poly-ethers of Trimethylene Glycol. C. A. ROJAHN (*Ber.*, 1921, **54**, [B], 3118—3121).—During the purification of trimethylene glycol (this vol., i, 105) considerable quantities of residue are obtained in which the presence of poly-ethers of trimethylene glycol was suspected. Attempts to isolate a uniform substance therefrom by fractionation under diminished pressure did not give entirely satisfactory results owing to the continuous formation of resin, but the molecular weights of the individual fractions in boiling alcohol pointed to the conclusion that they contained di- to hexa-ethers. Further purification was attempted by conversion of the individual fractions into the corresponding phenylurethanes (which was only successful with the fraction of molecular weight corresponding with the di-ether), by acetylation and subsequent quantitative hydrolysis of the acetates and by fission of the ethers.

The diphenylurethane of di-trimethylene glycol ether, $C_{20}H_{24}O_5N_2$, crystallises in small, colourless needles, m. p. 104—105°.

The fraction, b. p. 130—170°/12 mm., yielded di-trimethylene glycol ether diacetate, $O(CH_2 \cdot CH_2 \cdot CH_2 \cdot OAc)_2$, a colourless, somewhat viscous liquid, b. p. 181—183°/52—54 mm., 265—270°/atmospheric pressure (slight decomp.), $d_{25}^{25} 1.0864$, which was hydrolysed to the corresponding di-ether, a colourless, syrupy liquid, b. p. 155—160°/15 mm., $d_{25}^{25} 1.064$. Similarly, the fraction b. p. 180—210°/12 mm., gave the diacetate of tri-trimethylene glycol ether, a colourless, viscous liquid, b. p. 238°/80 mm., $d_{25}^{25} 1.0546$.

Di-trimethylene glycol ether is decomposed by a boiling saturated solution of hydrogen bromide in glacial acetic acid and subsequent treatment of the product with alkali hydroxide solution into trimethylene glycol, which was identified as the di-benzoate, needles, m. p. 60—61°, thus establishing the constitution of the ether.

Protracted ebullition of trimethylene glycol under the atmospheric pressure leads to the formation of poly-ethers. H. W.

Derivatives of Acetylenic Erythritol [Hexinene- $\alpha\beta\epsilon\zeta$ -tetrol], $HO \cdot CH_2 \cdot CH(OH) \cdot C \equiv C \cdot CH(OH) \cdot CH_2 \cdot OH$. R. LESPIEAU (*Compt. rend.*, 1921, **173**, 1367—1369).—Chloroacetaldehyde reacts with the dimagnesium derivative of acetylene in the presence of ether to give a black, viscous mass, which, when further treated with bromine in chloroform solution, gives a product which crystallises after several months. It is $\alpha\zeta$ -dichloro- $\gamma\delta$ -dibromohexen- $\beta\epsilon$ -diol, $CH_2Cl \cdot CH(OH) \cdot CBr \cdot CBr \cdot CH(OH) \cdot CH_2Cl$, m. p. 141—142.5°. The black, viscous mass mentioned above when treated with solid potassium hydroxide in ether gives the dioxide, $\begin{matrix} CH_2 \\ | \\ O \end{matrix} > CH \cdot C \equiv C \cdot CH < \begin{matrix} CH_2 \\ | \\ O \end{matrix}$, b. p. 87.5—88.5°/10 mm., $d_0 1.417$.

W. G.

Alkylations. I. Alkylation of Sodium Sulphite. H. BAGGESGAARD-RASMUSSEN and SVEN WERNER (*Bull. Soc. chim.*, 1921, [iv], 29, 1073—1087).—A quantitative study of the interaction of methyl or ethyl iodide and sodium sulphite in 30% methyl alcohol shows that the reaction is essentially bimolecular, although the curve is somewhat irregular towards the end. The abnormal progress of the reaction may be explained on the basis that in solution sodium sulphite exists in two tautomeric forms, which are in equilibrium, $\text{NaSO}_3\cdot\text{ONa} \rightleftharpoons \text{SO}(\text{ONa})_2$, and that only the first undergoes alkylation, the atom of sodium attached to sulphur being replaced by the alkyl group. The results indicate that, in solution, 88% of the sodium sulphite is in the first form and 12% in the second. W. G.

Neutralisation of the Affinity of Main and Subsidiary Valencies in Compounds of a Higher Order. III. J. V. DUBSKY [with P. APTEKMAN] (*J. pr. Chem.*, 1921, [ii], 103, 109—128; cf. A., 1916, i, 541).—Investigation of the behaviour towards pyridine of nickel salts of various substituted xanthic acids shows that the ability of xanthates of the general formula, $\text{OR}\cdot\text{CS}\cdot\text{SX}$, to form additive compounds with pyridine is independent of the volume of the radicle R, although the stability of the additive product diminishes with the magnitude of R. Unlike the cobalt xanthates previously investigated, cobalt amyl, benzyl, and bornyl xanthates unite with two molecules of pyridine, giving additive compounds far less stable than those given by the corresponding nickel salts.

It is not found possible to convert either tertiary alcohols, such as dimethylethylcarbinol, or phenols into the corresponding xanthic acid derivatives (cf. Meyer, "Analyse und Konstitutionsermittlung organischer Verbindungen," 3rd ed., 474), but analogous secondary alcohols, such as cyclohexanol or borneol, readily yield xanthic acid compounds. These results are in accord with those of Bamberger and Lodter (A., 1890, 517), who found that 5 : 6 : 7 : 8-tetrahydro-2-naphthol acts as a true phenol and gives no xanthate, whereas the isomeric 1 : 2 : 3 : 4-tetrahydro-2-naphthol behaves as a secondary alcohol (cf. Lippmann and Fleissner, A., 1888, 296).

Nickel propyl xanthate, $\text{Ni}(\text{CS}_2\cdot\text{OPr})_2$, forms brown crystals and gives with pyridine the compound $\text{C}_5\text{H}_{11}\text{O}_2\text{S}_4\text{Ni}_2\text{C}_5\text{H}_5\text{N}$, which separates in pale green crystals and is unstable in the air. *Nickel butyl xanthate*, $\text{Ni}(\text{CS}_2\cdot\text{O}\cdot\text{CH}_2\text{Pr})_2$, forms brown crystals and gives a pale green compound with 2 molecules of pyridine. *Nickel amyl xanthate*, $\text{Ni}(\text{CS}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Pr})_2$, crystallises in brown leaflets with a greenish-yellow lustre and forms a pale green compound with 2 molecules of pyridine. Cobalt amyl xanthate gives an unstable, brown compound with 2 molecules of pyridine. *Nickel cetyl xanthate*, $\text{Ni}(\text{CS}_2\cdot\text{O}\cdot[\text{CH}_2]_{15}\cdot\text{CH}_3)_2$, crystallises in orange-yellow leaflets, and forms a very unstable, green compound with 2 molecules of pyridine. *Cobalt cetyl xanthate* forms green crystals. *Sodium benzyl xanthate*, $\text{NaCS}_2\cdot\text{O}\cdot\text{CH}_2\text{Ph}$, and the *potassium* salt, were prepared. *Cobalt benzyl xanthate*, $\text{Co}(\text{CS}_2\cdot\text{O}\cdot\text{CH}_2\text{Ph})_2$, forms lustrous, black crystals.

gives a deep green solution in benzene, and with 2 molecules of pyridine yields a brown compound which is highly unstable, even in an atmosphere of pyridine. *Nickel benzyl xanthate* forms black crystals and with 2 molecules of pyridine yields a compound which remains unchanged in an atmosphere of pyridine. *Potassium cyclohexyl xanthate*, $\text{KCS}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_{11}$, is crystalline, and the *nickel* salt, $\text{Ni}(\text{CS}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_{11})_2$, forms brown crystals. *Sodium bornyl xanthate*, $\text{NaCS}_2 \cdot \text{O} \cdot \text{C}_{10}\text{H}_{17}$, is crystalline; the *nickel* salt forms brown crystals, and the cobalt salt forms with 2 molecules of pyridine a highly unstable, brown, crystalline compound.

T. H. P.

$\beta\beta'$ -Dichlorodiethyl Ether. The Oxygen Analogue of Mustard Gas. OLIVER KAMM and JOHN H. WALDO (*J. Amer. Chem. Soc.*, 1921, **43**, 2223—2227).— $\beta\beta'$ -Dichlorodiethyl ether, b. p. 177—178° (corr.); d_4^{20} 1.213; n_D^{20} 1.457, may be prepared by the action of concentrated sulphuric acid on ethylene chlorohydrin. When condensed with aniline, it gives 4-phenylmorpholine. When condensed with ethyl malonate, the ether gives *ethyl tetrahydropyran-4 : 4-dicarboxylate*, $\text{O} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C}(\text{CO}_2\text{Et})_2$, b. p. 260°/740—745 mm.; d_4^{20} 1.107, which with carbamide in the presence of sodium ethoxide yields *tetrahydropyran-4 : 5-spiro-2 : 4 : 6-triketohexahydropyrimidine*, $\text{O} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{C} \cdot \text{O}$, m. p. 218°.

$\beta\beta'$ -Dichlorodiethyl ether, unlike its sulphur analogue, exerts no deleterious action on the tissues of the animal body. Similarly, tetrahydropyran-4 : 5-spiro-2 : 4 : 6-triketohexahydropyrimidine, although closely related in structure to barbitol, possesses no marked hypnotic properties.

W. G.

$\gamma\gamma'$ -Dihalogenodipropyl Ethers. OLIVER KAMM and WALTER H. NEWCOMB (*J. Amer. Chem. Soc.*, 1921, **43**, 2228—2230).— $\gamma\gamma'$ -Dichlorodipropyl ether, b. p. 215°/745 mm.; d_4^{20} 1.140, was obtained by boiling trimethylene chlorohydrin with sulphuric acid under a reflux condenser.

Attempts to prepare trimethylene bromohydrin from trimethylene glycol by the action of hydrobromic acid and sulphuric acid gave a mixture of $\alpha\gamma$ -dibromopropane, the required bromohydrin and $\gamma\gamma'$ -dibromodipropyl ether, b. p. 128°/19 mm.; d_4^{20} 1.574. The products can be separated by fractional distillation.

W. G.

Preparation of β -Chloro- and β -Bromo-propionic Acids from Trimethylene Glycol. C. A. ROJAHN (*Ber.*, 1921, **54**, [B], 3115—3118).—Trimethylene glycol is present in considerable amount in the sweet water concentrates obtained by the fermentation of sugar to glycerol by the method of Connstein and Lüdecke, particularly when the operation is conducted with insufficient care. It is purified by distillation, dilution of the fraction, b. p. 170—230°, with water, and treatment of the hot solution with lead oxide and barium hydroxide in a current of air. After removal of lead and barium by sulphuric acid, air is passed through

the hot solution whereby the bulk of the organic acids are removed and trimethylene glycol, b. p. 210° , d_4^{25} 1.0573, is ultimately isolated by repeated distillation, finally under diminished pressure. It is treated at the temperature of boiling water with about two-thirds of the calculated quantity of hydrogen chloride, and the product is fractionated, giving thereby (i) water and dichloropropane, (ii) γ -chloropropyl alcohol, (iii) unchanged trimethylene glycol, and (iv) a residue (see this vol., i, 103). β -Chloropropyl alcohol is added gradually to nitric acid (30%) at 0° , and the mixture maintained at below 5° during twenty-four hours, after which it is cautiously treated at $30-35^{\circ}$, allowed to remain during eight hours, and subsequently heated at $70-75^{\circ}$; β -chloropropionic acid, colourless needles, m. p. $37-38^{\circ}$, is thus formed in 30-40% yield.

Trimethylene glycol is converted by boiling hydrobromic acid into a mixture of $\alpha\gamma$ -dibromopropane and γ -bromopropyl alcohol. The latter is oxidised by nitric acid to β -bromopropionic acid, b. p. $140-142^{\circ}/45$ mm., m. p. $62-63^{\circ}$; the action proceeds less violently than with γ -chloropropyl alcohol.

H. W.

The Mixed Anhydrides of Sulphuric Acid and Carboxylic Acids. II. *n*-Butyrylsulphuric Acid. A. J. VAN PESKI (*Rec. trav. chim.*, 1921, 40, 736-746; cf. A., 1921, i, 302).—*n*-Butyrylsulphuric acid, $C_4H_7CO\cdot O\cdot SO_3H$, is formed by the action of sulphur trioxide on *n*-butyric acid, and resembles acetylsulphuric acid in its general properties. When heated, it is transformed into α -sulphobutyric acid, and at 70° evolution of carbon dioxide takes place with sharp rise in temperature to about 110° , the other product being α -sulphobutyron. Full experimental details are given as to the preparation of the acid, its sodium salt, and, from the latter, of butyric anhydride, the preparation of isoamylsulphuric acid, phenyl butyrate, tribromobutyranilide (long needles, m. p. 167.8°), tribromobutyrophenol (a pale yellow viscous liquid, m. p. $6-9^{\circ}$, b. p. $192.8^{\circ}/16$ mm. corr.) are described and also the sulphonation of benzene by the acid.

H. J. E.

C_{18} Fatty Acids. II. The Relation of Oleic and Elaidic Acids to their Halogen Additive Products. BEN H. NICOLET (*J. Amer. Chem. Soc.*, 1921, 43, 2122-2125; cf. A., 1921, i, 390).—Using the anilides of the various acids as means of characterising them, it is shown that there is no *cis-trans*-isomerisation when bromine is added to the double bond and later removed by zinc and alcoholic hydrochloric acid in the case of oleic or elaidic acids. These acids thus differ from linolic acid in this respect. *Oleanilide dibromide* has m. p. 67° ; *claidanilide dibromide* has m. p. 88° .

W. G.

The Mechanism of the Oxidation of Drying Oils as Elucidated by a Study of the True Oxygen Absorption. III. The Action of Driers. SAMUEL COFFEY (*T.*, 1922, 121, 17-23).

The Formation of Substituted Succinic Acids from Esters of $\alpha\beta$ -Unsaturated Acids. LUCY HIGGINBOTHAM and ARTHUR LAFWORTH (*T.*, 1922, 121, 49-54).

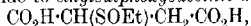
Nitromalic Acid. ARTHUR LACHMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 2084—2091; cf. A., 1921, i, 303).—*Nitromalic acid*, m. p. 110—112°, is readily obtained by adding fuming sulphuric acid to a cooled solution of malic acid in nitric acid (*d* 1.42). It gives a *sodium* and a *silver* salt. When hydrolysed with sodium hydroxide in aqueous solution, it yields a mixture of nitric and nitrous acids, the percentage of nitrous acid being independent of the temperature, the concentration, or the presence of an excess of alkali. Similar results were obtained in methyl alcoholic solution, except that the amount of nitrous acid obtained was nearly twice that in aqueous solution. When alkali was excluded altogether and a substance such as sulphanilic acid, capable of reacting with the nitrous acid as fast as it is formed, was present, the production of nitrous acid was greatly increased and the rate under these conditions corresponded with a unimolecular reaction.

In the hydrolysis of nitric esters, two independent processes occur. One is the normal hydrolysis into alcohol or hydroxy-acid and nitric acid, and the second is isomerisation to a nitrous ester, which subsequently is hydrolysed to an aldehyde or a ketone. Each of these reactions proceeds at its own rate under given conditions. The action of alcohol in increasing the yield of nitrous acid is that it diminishes the rate of the normal hydrolysis of the nitric ester to nitric acid. The constant yield when alkali is employed is a false equilibrium. The real constant is the ratio of the velocities of the two reactions. W. G.

Stereoisomeric Ethylthiolsuccinic Acids. PETER FITGER (*Ber.*, 1921, **54**, [B], 2943—2951).—*r-Ethylthiolsuccinic acid*, $\text{CO}_2\text{H}\cdot\text{CH}(\text{SEt})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, small, colourless needles, m. p. 124—126°, is prepared from ethyl mercaptan, sodium bromosuccinate, and sodium hydroxide in aqueous solution or by the action of ethyl bromide and sodium hydroxide on sodium thiolsuccinate dissolved in water. The normal salts, with the exception of those of *silver*, *lead*, and *iron*, are generally freely soluble in water; the *sodium hydrogen*, *potassium hydrogen*, and *barium hydrogen* salts crystallise in colourless prisms. Attempts to resolve the racemic acid into its optically active components by means of the phenyl-ethylamines were unsuccessful, since a partly racemic salt is the least soluble. On the other hand, a partly active *d*-acid could be obtained by the action of ethyl mercaptan and sodium hydroxide on an aqueous solution of sodium *l*-bromosuccinate, and from this the pure *d*-variety could be isolated with the aid of *d*-phenyl-ethylamine. *d-Ethylthiolsuccinic acid*, m. p. 126—128°, forms lustrous aggregates of prisms or needles; it has $[\alpha]_D^{20} + 139.3^\circ$ in absolute alcohol, $[\alpha]_D^{20} + 149.8^\circ$ in ethyl acetate, $[\alpha]_D^{20} + 145.0^\circ$ in acetone, $[\alpha]_D^{20} + 107.7^\circ$ in water. Under certain conditions, it is possible to isolate the almost pure *d*-acid by the process described above in relatively good yield and without recourse to *d*-phenyl-ethylamine. *l-Ethylthiolsuccinic acid* is obtained in good yield by the action of ethyl bromide and sodium hydroxide on an aqueous

solution of sodium *l*-thiolsuccinate; it forms aggregates of lustrous needles, m. p. 126–128°, $[\alpha]_D^{25}$ –139.3° in absolute alcohol, $[\alpha]_D^{25}$ –150.0° in ethyl acetate, $[\alpha]_D^{25}$ –145.1° in acetone, $[\alpha]_D^{25}$ –108.0° in water. It was not found possible to isolate well-defined salts of the active acids. H. W.

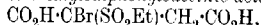
Certain Products of the Oxidation of Inactive Ethylthiol-succinic Acid. PETER FITGER (*Ber.*, 1921, **54**, [B], 2952–2963; cf. preceding abstract).—Ethylthiolsuccinic acid is oxidised by hydrogen peroxide to *ethylsulphoxysuccinic acid*,



which becomes discoloured at 120°, but does not exhibit a definite melting point when more strongly heated. The *ferric* and *silver* salts are described, but, in general, the normal salts do not appear to be sharply characterised. The acid is unstable when dissolved in water or ethyl acetate, and in boiling solution becomes decomposed into carbon dioxide, ethyl mercaptan, diethyl disulphide, fumaric acid, and β -ethylthiolacrylic acid, long, colourless, slender needles, m. p. 83–84°.

Sodium ethylthiolsuccinate is oxidised by potassium permanganate in aqueous solution, and in the presence of carbon dioxide to *r*-ethylsulphonylsuccinic acid, long, colourless prisms, m. p. 167–168°; the *sodium* salt, $\text{C}_6\text{H}_8\text{O}_6\text{SNa}_2\cdot 2\text{H}_2\text{O}$, colourless, rhombic plates, *barium* salt, pointed prisms, *silver* salt (+2H₂O), prisms, and *ferric* salt are described.

The action of bromine on an aqueous solution of *r*-ethylthiolsuccinic acid appears to lead to the initial formation of ethylsulphoxysuccinic acid (which is too unstable to permit its isolation in these circumstances), and then to ethylsulphonylsuccinic acid, which can only be prepared in poor yield in this manner. The use of three molecular proportions of bromine, on the other hand, readily gives α -bromo- α -ethylsulphonylsuccinic acid,



colourless, microscopic plates (+H₂O), m. p. 83–85° (decomp.); the *silver*, *ferric*, and *barium* (+3H₂O) salts are described. The acid readily eliminates carbon dioxide in hot aqueous acidic solution and passes into β -bromo- β -ethylsulphonylpropionic acid, colourless prisms, m. p. 142–143° (decomp.); the *ferric* salt and *silver* salt, needles, are described.

Ethylthiolsuccinic acid, when dissolved in glacial acetic acid, reacts vigorously with bromine, giving α -bromo- β -ethylthiolmaleic acid, $\text{CO}_2\text{H}\cdot\text{CBr}(\text{SEt})\cdot\text{CO}_2\text{H}$, pale yellow, thin plates or flattened prisms, m. p. 131° to 141° (decomp.), according to the mode of heating. The *barium* salt, voluminous needles, and the *anhydride*, long, pale yellow needles, m. p. 44–45°, are described.

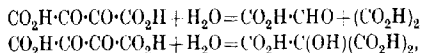
Ethylthiolsuccinic acid is extensively decomposed by potassium permanganate in bicarbonate-alkaline solution, but the products formed have not yet been identified. H. W.

Behaviour of Fehling's Solution in Light. A. BENRATH and J. OBERBACH (*Z. physikal. Chem.*, 1921, **98**, 498–501).—The

authors have been unable to confirm the statement of Bolin and Linder (A., 1920, ii, 144) that when Fehling's solution contained in glass vessels is exposed to ultra-violet light no reaction occurs. It is found that Fehling's solution exposed in a glass tube to sunlight is decolorised, with the evolution of hydrogen. Illumination of an alkaline solution of potassium sodium tartrate gives no evolution of gas, but if cuprous oxide is added, hydrogen is vigorously evolved; copper turnings and even massive copper have the same action. Fehling's solution to which copper has been added evolves hydrogen immediately it is exposed to light, and the action persists for some time after the light is removed. The oxidation products of tartaric acid, such as dihydroxytartaric acid, mesoxalic acid, and formic acid, when treated with alkali hydroxides and metallic copper, evolve hydrogen in light. Mesoxalic acid has the most pronounced action, and the insoluble sodium dihydroxytartrate passes into solution with the evolution of hydrogen. If dihydroxytartaric acid is added to Fehling's solution, it is decolorised more rapidly than if the addition has not been made. In all cases where the reaction was carried out in quartz vessels, a thin deposit of copper was found on the walls of the vessel. The reaction probably follows the course: the Fehling's solution decomposes in light, forming cuprous oxide and metallic copper, and these act catalytically on the tartaric acid, producing hydrogen and oxidation products of tartaric acid. Some of the oxidation products are further oxidised in the dark.

J. F. S.

Dihydroxytartaric Acid. ARTHUR LACHMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 2091—2097; cf. Fenton, T., 1898, **74**, 71; 1902, **81**, 426).—Dihydroxytartaric acid, considered as a diketone, has a structure similar to benzil, and when acted on by alkalis behaves like benzil, and thus its decomposition is represented by the equations



the carboxytartronic acid losing carbon dioxide and giving tartronic acid. It is shown that when sodium dihydroxytartrate is heated at 160°, carbon dioxide is evolved and glyoxylic acid and oxalic acid were identified along with tartronic acid in the products of decomposition.

In Fenton's method for the estimation of sodium by precipitation as sodium dihydroxytartrate and subsequent oxidation of this salt with standard permanganate, it is necessary to carry out the oxidation first in alkaline and then in acid solution in order to obtain consistent results.

W. G.

Internal or Catalytic Dehydroxidation of Formaldehyde. ERICH MÜLLER (*Z. Elektrochem.*, 1921, **27**, 558—563).—Alkaline solutions of formaldehyde, when treated with oxidising agents such

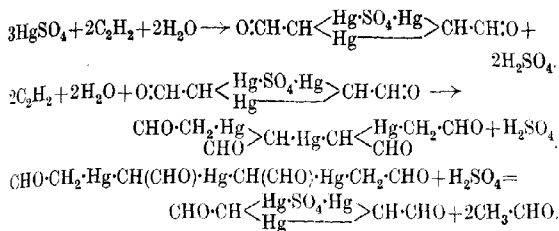
e*

as cuprous oxide, cupric oxide, silver oxide, potassium persulphate, hydrogen peroxide, or potassium ferricyanide, are converted into formic acid with evolution of hydrogen. The same reaction occurs on electrolysis of an alkaline solution of formaldehyde, and, finally, finely divided metals (Cu, Ag, Pd, Pt.), when added to alkaline solutions of formaldehyde, bring about a rapid evolution of hydrogen and formation of formic acid. The catalytic change is best shown with colloidal rhodium, thus: If to 30 c.c. of 15*N*-sodium hydroxide and 50 c.c. of 20% formaldehyde 20 c.c. of colloidal rhodium (0.05 gram) are added at 25°, there is an evolution of 3 litres of hydrogen in two hours. The author explains the electrolytic reaction as follows: In solution, formaldehyde exists in equilibrium as represented by the equations $\text{HCHO} + \text{H}_2\text{O} \rightleftharpoons \text{HCH}(\text{OH})_2 \rightleftharpoons \text{HCHO}'(\text{OH}) + \text{H}'$, on the anode the reaction $\text{HCH}(\text{OH})\text{O}' + \text{F} = \text{HCH}(\text{OH})\text{O}$ takes place; this substance the author terms an O-aldehyde, and states that it may exist in the metastable condition in formaldehyde solution up to a definite concentration. Above this definite concentration, it spontaneously decomposes to give hydrogen and formic acid, $\text{H}\cdot\text{CH}(\text{OH})\text{O} \rightarrow \text{HC}(\text{OH})\text{O} + \text{H}$, but at lower concentrations it is decomposed only by oxidising agents or catalysts. This reaction the author terms "dehydroxidation." The course of the reaction with catalysts is represented as follows: In alkaline solution, a reaction similar to Cannizzaro's reaction occurs in two stages, (1) $3\text{HCHO} + 2\text{H}_2\text{O} = \text{CH}_3\text{OH} + 2\text{HCH}(\text{OH})\text{O}$ and in the presence of the catalysts (2) $2\text{HCH}(\text{OH})\text{O} = 2\text{HCO}_2\text{H} + \text{H}_2$. J. F. S.

Alcoholic Fermentation of Formaldehyde by Osmium.

ERICH MÜLLER (*Ber.*, 1921, **54**, [B], 3214—3216).—An aqueous solution of formaldehyde decomposes in the presence of osmium into carbon dioxide and methyl alcohol. The catalytic activity of the metal diminishes somewhat rapidly. At about 50°, and then only to a small extent, hydrogen is also evolved. H. W.

The Rôle of Mercury Salts in the Catalytic Transformation of Acetylene into Acetaldehyde and a New Commercial Process for the Manufacture of Paracetaldehyde. RICHARD R. VOGT and JULIUS A. NIEUWLAND (*J. Amer. Chem. Soc.*, 1921, **43**, 2071—2081).—In the commercial preparation of acetaldehyde from acetylene and water by the use of mercury salts as catalysts, the chief drawback is the ease with which the mercury salt is reduced to metallic mercury, with consequent loss in activity. It is now shown that mercuric sulphate in sulphuric acid is the most suitable catalyst, on account of its activity and less ready reduction, but the difficulty attached to its use is the impossibility of separating acetaldehyde from the more concentrated acid solution and the rapid reduction of the mercury compounds in dilute acid solutions. In such solutions, the mercury is soon converted into an organic compound, and this compound acts as the catalyst. It is suggested that the reaction may be as follows:



It is considered that the reduction of mercury compounds by acetylene is in some way due to their hydrolysis in dilute acid solutions, and the only way in which acetaldehyde could be obtained without the reduction of any mercury salt whatever was by the action of a stream of moist acetylene at 70—120° on a dry mixture of the mercuric sulphate-acetylene compound and sodium, potassium, or ammonium hydrogen sulphates. This process was, however, so slow as not to be of practical value.

Owing to the difficulty of obtaining the acetaldehyde from these acid solutions, it was found advantageous to use the solutions in place of pure acetaldehyde in the preparation of quinaldine. For this purpose, aniline sulphate was dissolved along with the mercuric sulphate in sulphuric acid before passing in the acetylene, a concentration of 40% of sulphuric acid and a temperature of 60° being most advantageous.

For the preparation of paracetaldehyde, a large bottle or carboy was filled with dry fragments of glass on which a pasty mass of mercuric sulphate, sodium or ammonium hydrogen sulphate, and a very little water was distributed and the moist acetylene led in with shaking. The paracetaldehyde accumulated as a separate layer at the bottom of the bottle. The aldehyde-mercury ratio obtained was 17:1 with a steady production of paracetaldehyde. In this method no distillation process is necessary, there are no by-products or waste products, and there is no excess of acetylene to be recovered.

W. G.

Preparation of Aldol from Acetaldehyde. NATHAN GRÜNSTEIN (Brit. Pat. 147119).—Aldol condensation by means of a very small quantity of an alkaline catalyst proceeds, without the addition of ice or a neutral organic diluent, as a smooth and easily controlled reaction if the acetic acid contained in the acetaldehyde is first neutralised with the requisite quantity of sodium hydroxide solution, and the catalyst is then gradually added with cooling, the operation being preferably conducted in an atmosphere of nitrogen to prevent the formation of further quantities of acetic acid by atmospheric oxidation. As catalyst, aqueous alkali hydroxide, not exceeding in quantity 1 part of alkali to 100 parts of acetaldehyde, may be employed, or equally favourable results are obtained with alkali or alkaline-earth carbides or cyanides, or alkaline-earth hydroxides. In all cases, the presence of a small

quantity of water appears to be essential. To prevent the condensation proceeding too far with formation of resins, etc., it is stopped before all the acetaldehyde has been converted into aldol by adding sufficient hydrochloric or acetic acid to neutralise the alkali, separating the salt, and distilling the product in a vacuum.

G. F. M.

Preparation of Butaldehyde and Butyl Alcohol from Crotonaldehyde. NATHAN GRÜNSTEIN (Brit. Pat. 147118).—

Butaldehyde and butyl alcohol are obtained in good yield by the catalytic hydrogenation of crotonaldehyde in presence of 20–25% of water or steam. The formation of undesirable by-products of high boiling point is greatly minimised by using a large excess of hydrogen, and the excess passing from the catalyst can be recirculated after suitable cooling to condense the reaction products. The catalyst is prepared by depositing in the usual manner 5–15 parts of nickel on 100 parts of pumice or kieselguhr, and the optimum temperature for the hydrogenation is 110–120°. Instead of using a mixture of pure crotonaldehyde and water, the product of the decomposition of aldol may be employed with equal advantage. The reaction may be carried out either in a tube charged with the contact material, or with the liquid substances in an autoclave, the hydrogen in the latter case being pumped in at 10–15 atm. pressure with vigorous agitation of the liquid. In either case, provision must be made for the periodical discharge of gas from the apparatus as the hydrogen becomes contaminated with propylene and carbon monoxide produced by the “cracking” of the crotonaldehyde, particularly at the higher temperatures.

G. F. M.

Benzyl Ethers of Carbohydrates. M. GOMBERG and C. C. BUCHLER (*J. Amer. Chem. Soc.*, 1921, **43**, 1904–1911).—Carbohydrates of all types are readily benzylated and various benzyl ethers obtained when the carbohydrate is heated with benzyl chloride and aqueous sodium hydroxide for several hours at about 90°. Thus α -methylglucoside yielded benzylglucoside, *dibenzylmethylglucoside*, and *tetrabenzylbenzylglucoside*. Sucrose gave a solid *dibenzyl* and a liquid *pentabenzyl* derivative. Dextrin gave a *benzyl*dextrin, $C_{12}H_{18}O_{10} \cdot C_7H_7$, m. p. 208–210°; potato starch gave a *monobenzyl* derivative, $C_{12}H_{18}O_{10} \cdot C_7H_7$, m. p. 200–203°, and maize starch gave a *dibenzyl* derivative, $C_{12}H_{18}O_{10} (C_7H_7)_2$, m. p. 203–205°. Cellulose, unless previously subjected to one of the several so-called “hydration” processes, underwent only slight benzylation, but after hydration a *monobenzyl*, a *tribenzyl*, and a *tetrabenzyl* derivative were obtained according to the conditions. Benzylated cellulose, unlike cellulose itself, is insoluble in Schweizer's reagent.

W. G.

Biochemical Synthesis of α -Methyl-*d*-mannoside. H. HÉRISSEY (*Compt. rend.*, 1921, **173**, 1406–1407; cf. A., 1921, i, 306).—By the action of α -methyl-*d*-mannosidase, present in the

germinated seeds of lucerne, on a solution of mannose in 10% methyl alcohol, the author has synthesised α -methyl-*D*-mannoside and obtained it in a crystalline form. W. G.

The Formation of Osazones. MARC H. VAN LAER and R. LOMBAERS (*Bull. Soc. chim. Belg.*, 1921, **30**, 296–301).—A study of the formation of the osazones of lævulose and dextrose shows that the difference in the time of the reaction has its origin at the second stage and is due to the fact that the oxidation by the second molecule of phenylhydrazine is, in the first case, that of a primary alcohol, and, in the second, that of a secondary one. H. J. E.

Pentosans. EMIL HEUSER (*J. pr. Chem.*, 1921, [ii], **103**, 69–102).—[With MARIA BRADEN.]—Salkowski's method for the preparation of xylan from wheat straw (*A.*, 1902, i, 206) yields a product which gives at most 80% of the theoretical proportion of furfuraldehyde and contains appreciable amounts of ash. The author finds that application of a modification of Salkowski's method to bleached straw cellulose [*Strohzellstoff*] (cf. Heuser and Haug, *Z. angew. Chem.*, 1918, **31**, 99) is capable of yielding a product containing 96% of xylan, calculated on the dry ash-free material, and 0.35% of ash.

[With E. KÜRSCHNER.]—By 43% hydrochloric acid solution (*d* 1.21) at the ordinary temperature, xylan cannot be hydrolysed completely to xylose, since part of the latter is destroyed before the hydrolysis is finished. The results obtained when the course of the hydrolysis is followed by measuring the copper-reducing power and by estimation of the furfuraldehyde obtained by treatment with hydrochloric acid show that no sugar other than xylose is formed during the hydrolysis, but fail to indicate the nature of the 4% of non-xylan in the preparation. [Cf. *J. Soc. Chem. Ind.*, 1922, Feb.] T. H. P.

Chemistry of Starch. IV. The Methylation of Poly-amyloses. HANS PRINGSHEIM and WALTER PERSCH (*Ber.*, 1921, **54**, [B], 3162–3168; cf. *A.*, 1912, i, 832; 1913, i, 1156; 1915, i, 382).—Tetra-amylose is not converted into a homogeneous product by sodium hydroxide and methyl sulphate. If, however, the material which is thus obtained, containing 28% OMe, is treated with methyl iodide and silver oxide, it gives a crystalline substance which contains two methoxyl groups in each dextrose residue. Very protracted treatment does not bring about methylation of the third hydroxyl group. The most important observation, however, is that the treatment does not cause depolymerisation, and that, in accordance with determinations of the molecular weight in freezing benzene or naphthalene, the product is to be regarded as *octamethyltetra-amylose*. It crystallises in colourless, hexagonal plates which do not decompose below 250° and has $[\alpha]_D^{20} +141.3$ to $+148.2^\circ$ in ethyl alcoholic solution. The slight mutarotation is somewhat surprising, since the original tetra-amylose is not mutarotatory.

Fermentation of starch by a degenerated specimen of *Bacillus*

macerans has led to the isolation of a tetra-amylose which gives a dark green, crystalline, additive compound with iodine, and, after being freed from the latter, a crystalline, additive product with carbon disulphide. Removal of the latter gives a tetra-amylose crystallising in needles and having a specific rotation higher by a few degrees than that quoted for previous specimens. The substance is possibly a stereoisomeride, but its preparation is difficult and uncertain.

H. W.

Preparation and Alkyl Interchange of Cellulose Esters; Cellulose Stearate and Laurate. AD. GRÜN and FRANZ WITTKA (*Z. angew. Chem.*, 1921, **34**, 645—648; cf. A., 1921, i, 222).—The attempt to find a simple method for the preparation of cellulose esters of the higher fatty acids has led to observations on the interchange of alkyl groups between cellulose esters and alcohols, and between alkyl esters and cellulose. Cellulose esters of the higher fatty acids are formed by acylation of cellulose with an acid chloride and pyridine. Preliminary experiments with stearyl chloride led to impure monostearate, and mixtures of cellulose mono- and di-stearate; the pure distearate was only obtained by the use of a large excess of the acid chloride, the reaction mixture being diluted with benzene. *Cellulose distearate* forms white fibres, m. p. 220° (decomp.), is insoluble in the usual cellulose solvents, even in an ammoniacal solution of copper oxide, but soluble in fatty acids and in glycerides on heating at about 200°. The fibres under the microscope are cylindrical and swollen to two or three times the original volume, and the lumen has partly disappeared. *Cellulose dilaurate* is a white, spongy, short-fibred mass, m. p. about 250°. The solubility in glycerides is greater than that of the distearate, and, when dissolved in triisovalerin and diluted with alcohol, a faintly coloured powder is obtained, m. p. 110°. Cellulose distearate and dilaurate exhibit a characteristic behaviour with fat colouring matters, for with Sudan-III an intense scarlet-red coloration is produced which is not removed by treatment with 50% alcohol, whereas cellulose or cellulose steeped in fatty acids is only faintly coloured, and the colour is completely removed by 50% alcohol. These cellulose esters may be distinguished further from cellulose by their behaviour with iodine and sulphuric acid, for they are coloured wine-red and the fibre swells but little, and is not disintegrated by the acid. The interchange of alkyl groups between ethyl esters of fatty acids and cellulose does not proceed as readily as with glycerol. Alkyl interchange between the cellulose esters of the lower fatty acids and alcohols proceeds readily, however, but the esters of the higher fatty acids react with difficulty. Thus, cellulose triacetate and ethyl alcohol yield cellulose monoacetate, whereas under similar conditions but little stearic acid is removed from cellulose distearate. The stability of the cellulose esters increases with their molecular weight. When isoamyl alcohol reacts with cellulose triacetate, alkyl interchange occurs, but is accompanied by a far-reaching degradation of the cellulose molecule.

F. M. R.

Plant Colloids. XII. Action of Formaldehyde on Cellulose. M. SAMEC and S. FERJANČIĆ (*Koll. Chem. Beihefte*, 1921, 14, 209—226; cf. A., 1921, i, 400, 707).—Purified sulphite cellulose has been heated under pressure with formaldehyde or formic acid at 143° for various periods of time and the products have been compared with the original cellulose. It is shown that formaldehyde reacts with cellulose and its derivatives when they have been converted into the emulsoid condition. The product does not give any iodine coloration, but after washing away the formaldehyde the colour can be obtained after the product has been emulsified by sulphuric acid. The sulpholysis of cellulose in the presence of formaldehyde takes place differently from the action in its absence and leads to low molecular derivatives. The charring of cellulose derivatives by strong sulphuric acid is strongly retarded by formaldehyde, and in the same way the esterification of cellulose derivatives is also retarded. Formaldehyde has a similar action on cellulose derivatives. The experimental results are explained by the assumption that the formaldehyde unites to the cellulose with the breaking of oxygen rings and the formation of oxymethylene groups, and that in the cellulose molecule an internal anhydride formation follows with the hydroxyl group of a neighbouring dextrose residue. J. F. S.

Alkaline Copper Hydroxide Solutions and Copper Oxide-Ammine-Cellulose Solutions. WILHELM TRAUBE (*Ber.*, 1921, 54, [B], 3220—3232).—The term "alkaline copper hydroxide solutions" is applied to the aqueous solutions produced from polyhydroxy-compounds, copper oxide or hydroxide, and alkali hydroxides. The quantity of copper hydroxide dissolved by solutions of glycerol and potassium hydroxide in which the concentration of the latter is maintained constant increases with increasing molecular ratio of alkali to glycerol within certain limits; it diminishes with increasing dilution of the alkali. Since copper hydroxide is not soluble in glycerol or in alkali hydroxide solutions of the concentration used, it appears that the action depends on the initial formation of alkali glyceroxide and reaction of the latter with copper hydroxide to give an alkali-copper glyceroxide. The behaviour of polyhydroxy-alcohols and of polyhydroxy-compounds in general is similar to that of glycerol. The place of the fixed alkalis can be taken by the ethylenediamine hydroxide of copper (A., 1912, i, 9), since it is found that addition of glycerol enables a solution of ethylenediamine saturated with copper hydroxide to dissolve considerably further amounts of the substance. A similar effect is produced by mannitol or sucrose. The solubility of cellulose in a solution of the ethylenediamine hydroxide of copper is also to be attributed to the formation of an alkoxide compound of the polyhydroxy-compounds produced by the degradation of cellulose, since it is found that a solution of ethylenediamine saturated with copper hydroxide has the power of dissolving more of the latter after being treated with cellulose. The ability to dissolve cellulose is, however, a specific

property of the copper solutions, since the ammine compounds of other metallic hydroxides, which in all probability are able to give rise to alkoxide derivatives, do not possess this power. The same conception of the solution of cellulose must be extended also to Schweizer's solution. Since copper hydroxide is relatively but little soluble in aqueous ammonia, it is not possible to obtain concentrated solutions of cellulose directly. Such solutions can, however, be obtained by taking advantage of the fact that Schweizer's solution saturated with cellulose has the power of dissolving further amounts of both cellulose and copper hydroxide. The explanation of the phenomenon is found in the existence in solution of an equilibrium, $\text{Cu}(\text{OH})_2 + 4\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4](\text{OH})_2$; in proportion as the ammine is removed in combination with cellulose or the products of its degradation, the equilibrium is displaced towards the right-hand side of the equation and further quantities of copper hydroxide can be dissolved. The insolubility of cellulose in copper ammine solutions which have been treated with glycerol is due to the fact that the copper is now present as the glyceroxide. The precipitation of cellulose from its solution in Schweizer's reagent by glycerol is likewise explained.

Soluble starch behaves towards alkaline copper hydroxide solution in the same manner as the other polyhydroxy-compounds. Ordinary starch swells and becomes intensely blue when brought into contact with ethylenediamine solution saturated with copper hydroxide; the colour is not removed by repeated washing with water. The substance contains nitrogen, and, possibly, is a well-defined compound of alkoxide nature.

H. W.

Cellulose. VI. De-polymerisation of Ethyl-cellulose.

KURT HESS and WALTER WITTELSBACH (*Ber.*, 1921, 54, [B], 3232—3241).—In a previous communication (*A.*, 1921, i, 710), the depolymerisation of ethyl-cellulose has been described and substances with a molecular weight in dilute solution of 800—900 have been isolated. Since, however, the molecular weight increased rapidly with increasing concentration owing to association, it remained doubtful whether still lower values would be observed in more dilute solution and the uncertainty was increased by the subsequent discovery (this vol., i, 12) of the ready conversion of cellulose by acetyl chloride into a compound of the composition and molecular weight of a biose-anhydride. It is now shown that the products of acetolysis of ethyl-cellulose, after action varying in its duration from two to one hundred and forty-four hours, have molecular weights in very dilute solution corresponding with those required for a tetraethylbiose anhydride. De-polymerisation of cellulose to "celluxose" occurs, therefore, with much greater readiness than has been assumed previously.

H. W.

Mercury Fulminate. HANS RATHSBURG (*Ber.*, 1921, 54, [B], 3185—3187).—The presence of unsaturated impurities in mercury fulminate can be detected by the behaviour of the

specimen towards potassium permanganate which is not affected by the pure compound. The amount of oxidising agent used by impure specimens depends on the medium in which they are suspended and, generally, is greatest in acid and least in aqueous suspension. On the other hand, the addition of halogen cannot be applied quantitatively, since pure mercury fulminate unites with halogen. Nevertheless, titration with iodine is a useful method of detecting the presence of more reactive mercury salts, which is judged by the presence of greater or less quantities of red mercuric iodide in the titrated mixture. The following process is more convenient than that advocated by Solonina for the estimation of oxalate in mercury fulminate. The specimen (about 3 grams) is dissolved in ammonia (20%) and the bulk of the fulminate, in so far as it is not decomposed, is re-precipitated with acetic acid. Oxalic acid is precipitated in the clear filtrate (or an aliquot portion thereof) with approximately *N*-calcium chloride and the calcium oxalate is weighed as such or as calcium oxide. H. W.

Preparation of Guanidine Nitrate. TENNEY L. DAVIS (*J. Amer. Chem. Soc.*, 1921, **43**, 2234—2238).—Guanidine nitrate may be obtained in excellent yield by heating dicyanodiamide with slightly more than two molecular proportions of ammonium nitrate for two hours at 160°, using either the dry materials alone or with water in an autoclave. At lower temperatures, diguanide nitrate is the main product. The reaction consists in the formation of diguanide nitrate by the action of one molecule of ammonium nitrate, and this then reacts with the second molecule of ammonium nitrate at the higher temperature to give guanidine nitrate.

The reaction is not therefore dependent on the depolymerisation of dicyanodiamide as suggested by Werner and Bell (*T.*, 1920, **118**, 1133) in their account of a similar preparation of guanidine thiocyanate. W. G.

The Synthesis of a Nitrogenous Principle of Plants, Hydrocyanic Acid, by the Oxidation of Ammonia and Carbohydrates, Glycerol, or Formaldehyde. R. FOSSE (*Compt. rend.*, 1921, **173**, 1370—1372; cf. *A.*, 1919, i, 152, 313, 459; 1920, i, 664, ii, 714, 779; 1921, i, 165, 321, 500, 652).—In the presence of a silver or a mercury salt, ammoniacal solutions of dextrose, sucrose, starch, dextrin, glycerol, or formaldehyde, on oxidation by potassium or calcium permanganate give cyanides as one of the products. W. G.

Synthesis of Hydrocyanic Acid by Oxidation, in Ammoniacal Silver Solution, of Alcohols, Phenols, and Amines. R. FOSSE and A. HIEULLE (*Compt. rend.*, 1922, **174**, 39—41).—It has been shown that, by the oxidation of a number of alcohols, phenols, and amines by potassium or calcium permanganate in ammoniacal solution in the presence of silver nitrate, hydrocyanic acid is always formed, but in variable amount. The highest yield of hydrocyanic acid was obtained from methylamine. W. G.

The Action of Aqueous Ammonia on Dicyanodiamide. TENNEY L. DAVIS (*J. Amer. Chem. Soc.*, 1921, **43**, 2230—2233).—When dicyanodiamide is heated in a sealed tube at 150° with aqueous ammonia (*d* 0.9) it gives, first, guanylearbamide and then guanidine carbonate. If the reaction is prolonged, the guanidine carbonate reacts with ammonia and carbon dioxide, giving in turn ammeline, ammeline, and, finally, melamine. W. G.

Organic Compounds of Arsenic. VII. Additive Compounds of Iodoform and Salts of Organic Bases of Tervalent Elements. WILHELM STEINKOPF and GUSTAV SCHWEN (*Ber.*, 1921, **54**, [B], 2969—2975; cf. this vol., i, 71, 72).—Attempts to convert tetramethylarsonium tri-iodide into the corresponding monoiodide by means of alcoholic potassium hydroxide solution have led to the isolation of an additive compound of molecular proportions of the latter and iodoform. Similar products can be obtained from quaternary ammonium, phosphonium, and stibinium iodides and, in certain cases, from the corresponding bromides. These compounds may also be produced from their components or from a mixture of the tertiary arsine, methyl iodide, and iodoform. They are pale yellow to yellow, crystalline substances which can be recrystallised without decomposition from organic solvents, but are decomposed by water with separation of iodoform. They are for the most part odourless. Their physiological action appears to be attributable to iodoform poisoning.

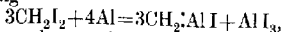
The following individual compounds are described. *Tetramethylarsonium iodide iodoform*, $I[Me_4As] \cdot 3CHI_3$, m. p. 165° (discoloration). *Phenyltrimethylarsonium iodide iodoform*, yellow needles, m. p. 143—145°, prepared by the methods indicated above or from phenyltrimethylarsonium hydroxide and iodoform in alcoholic solution. *Triphenylmethylarsonium bromide iodoform*, colourless crystals, m. p. 195°. *Triphenylmethylarsonium bromide iodoform*, pale brownish-yellow leaflets, m. p. 124°. *Tetramethylammonium iodide iodoform*, yellow needles, m. p. 237° after previous darkening when rapidly heated. *Tetraethylphosphonium iodide iodoform*, m. p. 212—215° after previous darkening when rapidly heated. [Tetraethylphosphonium bromide crystallises in colourless needles, m. p. about 320° (decomp.).] *Tetraethylphosphonium bromide iodoform*, brownish-yellow powder, m. p. about 200° after incipient decomposition at about 180°. *Tetraethylstibinium iodide iodoform*, yellow powder, m. p. (indefinite) 162° after previous softening.

It was not found possible to isolate additive compounds from iodoform and phenyltrimethylarsonium bromide or chloride, tetraethylammonium chloride, or triphenylmethylarsonium chloride, respectively. H. W.

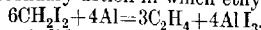
Some Recent Applications of Magnesium in Synthetic Organic Chemistry. HARRY HEPWORTH (*J. Soc. Chem. Ind.*, 1922, **41**, 7—11).—A résumé of some of the recent applications of the Grignard reagents,

Organo-derivatives of Thallium. III. Some Thallium-dialkyl Salts and the Preparation of Thalliumdiaryl Haloids.
 ARCHIBALD EDWIN GODDARD (T., 1922, 121, 36-40).

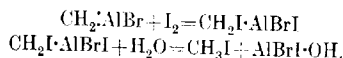
Mixed Organometallic Compounds of Aluminium.
 FAILLEBIN (*Compt. rend.*, 1922, 174, 112-114).—Aluminium dissolves in an anhydrous mixture of ether and methylene iodide, the reaction being



but there is a secondary action in which ethylene is formed,



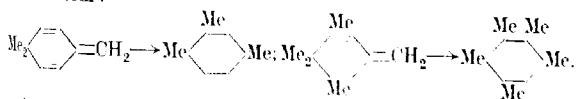
If the methylene iodide is replaced by methylene bromide, the action is more difficult to start and the secondary action is less marked. These complex compounds are obtained as dense liquids, which are readily decomposed by water, giving methane. A similar decomposition occurs with alcohol. The compounds are unsaturated and form additive compounds with iodine, which, when decomposed by water, no longer give methane but methyl iodide,



W. G.

Hydrocarbons of the Semibenzene Group. K. VON AUWERS and K. ZIEGLER (*Annalen*, 1921, 425, 217-280).—In continuation of previous work (Auwers and Müller, A., 1911, i, 621), a number of homologous semibenzene hydrocarbons have been prepared and examined with respect to their physical properties and their capacity for passing into aromatic hydrocarbons by isomeric change. The principal physical distinction between the semibenzene hydrocarbons and their aromatic isomerides consists in the fact that the former group of compounds have lower densities, and therefore (since the refractive indices of the two series are comparable) higher molecular refractions and dispersions than the latter. In general, the semibenzene compounds are more volatile than their isomerides.

The conversion of semibenzene hydrocarbons into benzene derivatives takes place in the presence of acids with great ease in the case of the simpler members. Higher in the series polymerisation and other side reactions occur simultaneously. In general, the isomeric change involves the migration of one methyl group from the *gem*-dimethyl residue to an adjacent position in the nucleus; but if both the neighbouring positions are already occupied the mobile group may attach itself to some other nuclear carbon atom:



A new series of physical constants for carefully purified 1:1-dimethyl-4-methylene- Δ^1 -cyclohexadiene is given: b. p. 38—

40°/15 mm., $d_4^{15.8}$ 0.8360, d_4^{20} 0.833, $n_D^{15.8}$ 1.50295, $n_D^{15.8}$ 1.51739, $n_D^{15.8}$ 1.53009, n_D^{20} 1.5011. This hydrocarbon passes into ψ -cumene with development of heat when a drop of hydrochloric acid is added to its solution in two vols. of acetic acid.

1:1-Dimethyl-4-ethyl- $\Delta^{2,5}$ -cyclohexadien-4-ol, large, transparent tablets, m. p. 46–47°, is prepared like the trimethyl compound (*loc. cit.*); on shaking with 10% sulphuric acid, it is converted into 1:1-dimethyl-4-ethylidene- $\Delta^{2,5}$ -cyclohexadiene, b. p. 71–74°/16 mm., 81.5–84°/25 mm., $d_4^{20.15}$ 0.8614, d_4^{20} 0.857, $n_D^{15.15}$ 1.51072, $n_D^{15.15}$ 1.51572, $n_D^{15.15}$ 1.53015, $n_D^{15.15}$ 1.54300, n_D^{20} 1.5135 (another preparation gave slightly different constants, e.g. d_4^{20} 0.855, n_D^{20} 1.5124). This hydrocarbon is fairly stable at 160°; on oxidation by permanganate, it is converted into dimethylmalonic acid and acetic acid. When its solution in acetic acid is saturated with hydrogen chloride, it is converted in the course of one hour into 1:2-dimethyl-4-ethylbenzene (b. p. 186–187°, $d_4^{15.2}$ 0.8777, d_4^{20} 0.874, $n_D^{15.05}$ 1.50103, $n_D^{15.05}$ 1.50489, $n_D^{15.05}$ 1.51606, $n_D^{15.05}$ 1.52531, n_D^{20} 1.5027), which was prepared for comparison from 4-*o*-xylol methyl ketone by reduction with amalgamated zinc and hydrochloric acid. 1:1-Dimethyl-4-*n*-propyl- $\Delta^{2,5}$ -cyclohexadien-4-ol and 1:1-dimethyl-4-*n*-propylidene- $\Delta^{2,5}$ -cyclohexadiene could not be fully purified (b. p. 95–105°/10 mm. and 83–85°, respectively). The crude alcohol was converted into 1:2-dimethyl-4-*n*-propylbenzene by the addition of a drop of concentrated hydrochloric acid to a solution in acetic acid, and the hydrocarbon identified by comparing its physical properties (b. p. 201–203°, $d_4^{25.5}$ 0.8718, d_4^{20} 0.866, $n_D^{15.27}$ 1.49504, $n_D^{15.27}$ 1.49881, $n_D^{15.27}$ 1.50920, $n_D^{15.27}$ 1.51784, n_D^{20} 1.4955) with those of a specimen prepared by reducing 4-*o*-xylol ethyl ketone. This ketone, b. p. 258–262°, was obtained by the action of propionyl chloride and aluminium chloride on *o*-xylene, and was characterised by means of its semicarbazone, m. p. 192–193°.

1:1:3:4-Tetramethyl- $\Delta^{2,5}$ -cyclohexadien-4-ol, needles, m. p. 50.5–51.5°, was obtained like its lower homologues, but could not be converted into the corresponding semibenzene owing to the ease with which this substance passed into its aromatic isomeride, durenene. From 1:1:3-trimethyl-4-ethyl- $\Delta^{2,5}$ -cyclohexadien-4-ol (m. p. 47–48°), however, 1:1:3-trimethyl-4-ethyl- $\Delta^{2,5}$ -cyclohexadiene (b. p. 85–86°, $d_4^{25.7}$ 0.8844, d_4^{20} 0.879, $n_D^{15.27}$ 1.51470, $n_D^{15.27}$ 1.51931, $n_D^{15.27}$ 1.53230, $n_D^{15.27}$ 1.54371, n_D^{20} 1.5160) was obtained by the usual means. It was converted by hydrochloric acid in the presence of acetic acid into 4-ethyl- ψ -cumene.

The following physical constants are recorded for 1:1:2:4-tetramethyl- $\Delta^{2,5}$ -cyclohexadien-4-ol: b. p. 90–95°, m. p. below 20°, $d_4^{10.9}$ 0.9333, d_4^{20} 0.925, $n_D^{10.1}$ 1.48376, $n_D^{10.1}$ 1.48685, $n_D^{10.1}$ 1.49502, $n_D^{10.1}$ 1.50176, n_D^{20} 1.4824. On treatment with acids it yields 1:1:2-trimethyl-4-methylene- $\Delta^{2,5}$ -cyclohexadiene (b. p. 60–65°/15 mm., $d_4^{19.7}$ 0.8735, d_4^{20} 0.866, $n_D^{10.7}$ 1.51331, $n_D^{10.7}$ 1.51813, $n_D^{10.7}$ 1.53213, $n_D^{10.7}$ 1.54435, n_D^{20} 1.5139), which readily passes into a polymeride. The isomeric aromatic hydrocarbon isodurenene is best obtained, therefore, from the alcohol.

1 : 1 : 3 : 4 : 6-Pentamethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol, b. p. 85—95°/12 mm., on dehydration gives 1 : 1 : 3 : 6-tetramethyl-4-methylene- $\Delta^{2:5}$ -cyclohexadiene, b. p. 77°/12 mm., d_4^{25} 0.8809, d_4^{20} 0.877, n_D^{25} 1.51235, $n_D^{15.2}$ 1.51687, $n_D^{13.2}$ 1.53006, $n_D^{12.2}$ 1.54172, n_D^{20} 1.5147, which isomerises, yielding pentamethylbenzene. 1 : 1 : 3 : 6-Tetramethyl-4-ethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol could not be purified by distillation owing to the ease with which it passes into 1 : 1 : 3 : 6-tetramethyl-4-ethylidene- $\Delta^{2:5}$ -cyclohexadiene. This hydrocarbon has the following constants: b. p. 100—103°/18 mm., d_4^{25} 0.8837, d_4^{20} 0.880, n_D^{25} 1.51028, $n_D^{13.4}$ 1.51452, $n_D^{12.4}$ 1.52702, $n_D^{12.4}$ 1.53796, n_D^{20} 1.5125.

The main product of the action of sodium hydroxide and chloroform on hemimellithenol is 1 : 2 : 6-trimethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one, m. p. 107.5—108.5°, which gives a semicarbazone, m. p. 218°, and a p-nitrophenylhydrazone, m. p. 190—191°. 6-Hydroxy-2 : 3 : 4-trimethylbenzaldehyde is a by-product in the reaction. It melts at 77—78° and yields a semicarbazone, which turns yellow at 130° but does not melt at 280°. Magnesium and methyl iodide convert the chloro-ketone into 1 : 2 : 4 : 6-tetramethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol, which, however, is partly decomposed during the isolation, giving 1 : 2 : 3-trimethyl-5-di-*o*-chloroethylbenzene, for which the following constants are recorded: b. p. 155—159°/19 mm., d_4^{25} 1.1424, d_4^{20} 1.144, n_D^{25} 1.53900, n_D^{15} 1.54310, n_D^{15} 1.55494, n_D^{20} 1.5439. On reducing the above chloro-alcohol, two substances are obtained, the normal product, 1 : 1 : 2 : 4 : 6-pentamethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol, having partly undergone dehydration with the formation of 1 : 1 : 2 : 6-tetramethyl-4-methylene- $\Delta^{2:5}$ -cyclohexadiene, which, when pure, has the following constants: b. p. 89—90°/15 mm., d_4^{25} 0.8765, d_4^{20} 0.879, n_D^{25} 1.50884, $n_D^{15.2}$ 1.51350, $n_D^{13.2}$ 1.52660, $n_D^{12.2}$ 1.53830, n_D^{20} 1.5149. When warmed with acetic acid and sulphuric acid, this hydrocarbon undergoes isomeric change with the formation of pentamethyl benzene.

C. K. I.

Constitution of Benzene. RONALD FRASER (T., 1922, 121, 188—196).

The Action of Sulphuryl Chloride on Organic Substances.
I. Simple Monosubstituted Benzenes. THOMAS HAROLD DURRANS (T., 1922, 121, 44—49).

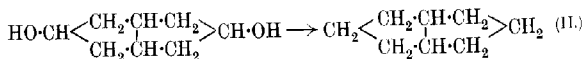
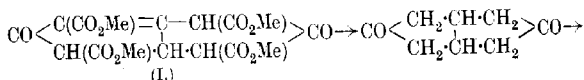
The Existence and Reactions of Positive Halogen attached to Carbon in Aromatic Compounds. BEN H. NICOLET (*J. Amer. Chem. Soc.*, 1921, 43, 2081—2084).—3-Iodo-*p*-toluidine, 4-iodoaniline, aceto-3-bromo-*p*-toluidide, and 3-iodo-4-hydroxybenzoic acid when boiled with 10% hydrochloric acid are hydrolysed with a readiness decreasing in the order named, in such a way that in part they replace their halogen by hydrogen and in part give di- or tri-halogenated derivatives. This is considered to be the best evidence yet offered for the existence of positive halogen attached to carbon in the benzene nucleus. It will be

noticed that, in all cases, the halogen is in a position *ortho* or *para* to a strongly negative group. In similar compounds, iodine is more positive than bromine, and more positive in *ortho*- than in *para*-compounds. Alkali is much less effective than acid in removing such positive halogens. In the presence of stannous chloride and acid, the halogen is abnormally readily removed, but resubstitution is prevented. W. G.

The Action of Pyrosulphuryl Chloride on Toluene. WILHELM STEINKOFF and KURT BUCHHEIM (*Ber.*, 1921, **54**, 2963—2968).—Pyrosulphuryl chloride reacts with toluene at 60° with evolution of hydrogen chloride and sulphur dioxide. The reaction product is a mixture from which the following substances have been isolated: Toluene-*p*-sulphonic acid, toluene-*p*-sulphonyl chloride, a mixture of dichlorotoluenes, and 4-chloro-3:4'-ditolylsulphone, fine needles, m. p. 136°, which is also formed by the interaction of *o*-chlorotoluene and toluene-*p*-sulphonyl chloride dissolved in light petroleum in presence of aluminium chloride at 55°.

A vigorous reaction ensues when toluene is added to a mixture of pyrosulphuryl chloride and aluminium chloride at -5° to 0°, with formation of toluene-*p*-sulphonic acid, *o*- and *p*-chlorotoluene, *pp*-ditolylsulphone, and a substance, needles, m. p. 215—217°, containing chlorine but no sulphur. F. M. R.

Hydrogenated Naphthalenes and their Transformations. I. G. SCHROETER (*Annalen*, 1922, **426**, 1—17).—[With G. VOSSEN.]—The condensation between chloral and methyl malonate leads to the formation of methyl 0:3:3-dicyclo- Δ^1 -octene-3:7-dione-2:4:6:8-tetracarboxylate (I), which can be converted by hydrolysis and reduction into 0:3:3-dicyclooctane-3:7-dione, 0:3:3-dicyclo-octane-3:7-diol, and, finally, 0:3:3-dicyclooctane (II) (b. p. 138°, d_4^{20} 0.8817, n_D^{20} 1.46632):



Closely related to this hydrocarbon (II) are the hydrogenated naphthalenes, certain of which, moreover, are more easily and cheaply prepared.

[With F. STAHL, H. HAEHN, and C. PRIGGE.]—Full working details are given of the preparation of tetrahydronaphthalene by reducing naphthalene by means of hydrogen at 180—200° and 5—15 atmospheres in the presence of nickel. The hydrocarbon, purified by regeneration from its sulphonic acid, has b. p. 100—101°/25 mm., 206.5° (corr.)/755 mm., d_4^{20} 0.971, n_D^{20} 1.5434.

C. K. I.

Hydrogenated Naphthalenes and their Transformations.**II. Nitro- and Amino-derivatives of Tetrahydronaphthalene.**

G. SCHROETER [with E. KINDERMANN, C. DIETRICH, C. BEYSCHLAG, CL. FLEISCHHAUER, E. RIEBENSAHM, and C. OESTERLIN] (*Annalen*, 1922, **426**, 17—83).—This paper describes the nitration of tetrahydronaphthalene, the reduction of various mono-, di-, and tri-nitro-derivatives, and the nitration of the acetyl derivatives of the amines so obtained. The orientations of a considerable number of isomeric nitro-compounds, amines, and nitroamines are definitely established.

The mononitration of tetrahydronaphthalene, using a mixture of nitric and sulphuric acids, leads to the formation of both 1- and 2-nitro-*ar-tetrahydronaphthalene* which may be separated by fractional distillation and "freezing out" the fractions or by taking advantage of the fact that the 2-nitro-compound is more easily reduced than its isomeride to an amino-derivative. 1-Nitro-*ar-tetrahydronaphthalene* has m. p. 34° , b. p. $157^{\circ}/13$ mm., d_4^{20} 1.1757 and the 2-compound, m. p. 31.4° , b. p. $169^{\circ}/13$ mm., d_4^{20} 1.1762. On dinitration, tetrahydronaphthalene yields a mixture of 1:2-dinitro-*ar-tetrahydronaphthalene* (m. p. $102-103^{\circ}$) and 1:3-dinitro-*ar-tetrahydronaphthalene* (m. p. 95°) which may be separated by crystallisation from concentrated sulphuric acid, in which the former is less soluble. The orientation of the 1:2-compound rests on its reduction to *ar-tetrahydro-1:2-naphthylenediamine* and 1-nitro-*ar-tetrahydro- β -naphthylamine* (see below), and that of the 1:3-isomeride on its oxidation to 3:5-dinitrophthalic acid and its reduction to the 1:3-diamine and the 1-nitro-3-amino-compound (see below). Another oxidative fission which the 1:3-dinitro-compound undergoes with nitric acid leads to the formation of β -o-carboxytrinitrophenylpropionic acid, which decomposes violently on heating and is characterised by analysis of its potassium hydrogen salt. 1:3-Dinitro-*ar-tetrahydronaphthalene* cannot be further nitrated, but the 1:2-isomeride may be converted into 1:2:4-trinitro-*ar-tetrahydronaphthalene*, m. p. $94.5-95^{\circ}$, the structure of which is established by its conversion into the triamino-derivative (see below). The other possible isomeride, namely, 1:2:3-trinitro-*ar-tetrahydronaphthalene* is not produced by direct nitration.

1:1-Hydrazo-*ar-tetrahydronaphthalene*, which is obtained by reducing 1-nitro-*ar-tetrahydronaphthalene* by means of zinc dust and alkali, forms colourless, slender needles, m. p. $181-183^{\circ}$, and on oxidation by permanganate is converted quantitatively into 1:1-azo-*ar-tetrahydronaphthalene*. The latter, which crystallises in glistening, red needles, m. p. $190-191^{\circ}$, may also be obtained along with 1:1-azoxy-*ar-tetrahydronaphthalene*, yellow needles, m. p. 184° , by reduction of the nitro-compound with zinc and alkali hydroxide under less energetic conditions. The benzidine conversion applied to hydrazotetrahydronaphthalene gives rise to 4:4'-diamino-1:1'-di-*ar-tetrahydronaphthyl*, m. p. $153-154^{\circ}$, the hydrochloride, hydrobromide, sulphate, and phosphate of which are described. The corresponding diazonium salt gives substantive dyes on coupling

with naphthionic acid, Neville and Winthers's α -naphtholsulphonic acid, crocein acid, H-acid, salicylic acid, chromotropic acid, " β -aminonaphtholsulphonic acid" and G-acid, 4:4'-*dihydrazino*-1:1'-*di-ar-tetrahydronaphthyl*, on reduction by means of stannous chloride, and 4:4'-*diethoxy*-1:1'-*di-ar-tetrahydronaphthyl*, colourless needles, m. p. 173°, on decomposing with ethyl alcohol. A basic by-product, consisting of colourless needles, m. p. 216°, and giving a *hydrochloride* which is easily soluble in water, is obtained in the preparation of 4:4'-diamino-1:1'-*di-ar-tetrahydronaphthyl*. Apparently it is 1:1'-*diamino*-2:2'-*di-ar-tetrahydronaphthyl*, because when heated its hydrochloride yields ammonium chloride and a carbazole-like base which may be separated in the form of its picrate.

ar-Tetrahydro- α -naphthylamine and *ar*-tetrahydro- β -naphthylamine are obtained from the corresponding nitro-compounds by catalytic reduction, and may also be obtained by reducing the crude mononitration product of tetrahydronaphthalene and separating the isomeric bases by taking advantage of the differences of solubility of their hydrochlorides in water, their methanedisulphonates in 96% alcohol, and the difference in the ease with which the bases are acetylated. *ar*-Tetrahydro- α -naphthylamine, b. p. 146°/12 mm., gives a hydrochloride which is more easily soluble than that of the β -derivative, and a *methanedisulphonate* which forms colourless leaflets soluble in 20 parts of hot water, 60 parts of cold water, and about six times as soluble in alcohol as the β -compound. With phthalic anhydride, the base gives a *phthalamic acid*, $C_{10}H_{11}NH \cdot CO \cdot C_6H_4 \cdot CO_2H$, colourless needles, m. p. 182–184° (decomp.), which on heating passes into the *phthalimide* (needles, m. p. 148–150°) by loss of water. *ar*-Tetrahydro- α -naphthylamine is more easily acetylated than the β -compound, and its acetyl derivative (m. p. 156°) on methylation by the action of methyl sulphate on its sodio-derivative gives the *acetyl* derivative of *ar-tetrahydro- α -naphthylmethylamine*, which has m. p. 70–72° and b. p. 182–185°/11 mm. The *hydrochloride* and *sulphate* of *ar-tetrahydro- β -naphthylamine* (b. p. 147–148°/13 mm., m. p. 38·5–39·5°) are sparingly soluble in cold water and the *methanedisulphonate* is rather sparingly soluble in alcohol. The *phthalamic acid* forms glistening needles, m. p. 156·5–158·5°, and the *phthalimide*, needles, m. p. 169–171°. The acetyl derivative (m. p. 102–104°) on methylation yields the *acetyl* derivative of *ar-tetrahydro- β -naphthylmethylamine*, needles, m. p. 67–69°.

The preparation of aceto-4-nitro-*ar-tetrahydro- α -naphthalide* by nitration of aceto-*ar-tetrahydro- α -naphthalide* has been described by Green and Rowe (T., 1918, 113, 958), but it is now shown that aceto-2-nitro-*ar-tetrahydro- α -naphthalide* (colourless needles, m. p. 184–185°) and aceto-3-nitro-*ar-tetrahydro- α -naphthalide* (colourless needles, m. p. 193°) are formed as by-products. 2-Nitro-*ar-tetrahydro- α -naphthylamine*, which is obtained by hydrolysis of its acetyl derivative, forms orange needles, m. p. 87–88°. Its constitution rests on its relationship to *ar-tetrahydro-1:2-naphthylenediamine* (see later). 3-Nitro-*ar-tetrahydro- α -naphthylamine*, prepared

by hydrolysis of its acetyl compound, forms yellow leaflets, m. p. 78°. It is identical with the product obtained by regulated reduction of 1:3-dinitro-*ar*-tetrahydronaphthalene.

The course pursued by the nitration of aceto-*ar*-tetrahydro- β -naphthalide varies with the conditions. If glacial acetic acid is the solvent, aceto-3-nitro-*ar*-tetrahydro- β -naphthalide, long, yellow needles, m. p. 134—135.5°, is the main product, whilst aceto-1-nitro-*ar*-tetrahydro- β -naphthalide, colourless needles, m. p. 128—129°, is produced only in small amount. On the other hand, if the nitration is carried out in the presence of concentrated sulphuric acid, the main product is aceto-4-nitro-*ar*-tetrahydro- β -naphthalide, which forms long, colourless needles, m. p. 194°, whilst the 3-nitro-compound is a by-product. 3-Nitro-*ar*-tetrahydro- β -naphthylamine, the constitution of which follows from its reduction to the diamine (see below), forms long, red needles, m. p. 125—127°. 1-Nitro-*ar*-tetrahydro- β -naphthylamine, red needles, m. p. 96°, is obtained, not only by hydrolysis of its acetyl derivative, but also by partial reduction of 1:2-dinitro-*ar*-tetrahydronaphthalene. The structure assigned is based on its reduction to the diamine which is known. 4-Nitro-*ar*-tetrahydro- β -naphthylamine, m. p. 55°, obtained by hydrolysis of its acetyl compound, is identical with the substance produced by partial reduction of 1:3-dinitro-*ar*-tetrahydronaphthalene. 1-Nitro-*ar*-tetrahydronaphthalene is obtained when the amino-group is eliminated by diazotisation and subsequent reduction.

Aceto-1:3-dinitro-*ar*-tetrahydro- β -naphthalide, colourless needles, m. p. 189—191°, is produced by further nitration of aceto-1-nitro-*ar*-tetrahydro- β -naphthalide and aceto-3-nitro-*ar*-tetrahydro- β -naphthalide and as a by-product in the dinitration of aceto-*ar*-tetrahydro- β -naphthalide. When it is prepared from the 3-nitro-compound an isomeride, $C_{12}H_{13}O_5N_4$, of unknown constitution and having no definite melting point (decomp. at about 215°) is also formed. 1:3-Dinitro-*ar*-tetrahydro- β -naphthylamine, which forms yellow needles, m. p. 166—168°, is obtained by hydrolysing the acetyl compound. On reduction, it yields 1:2:3-triamino-*ar*-tetrahydronaphthalene (below).

Aceto-3:4-dinitro-*ar*-tetrahydro- β -naphthalide, needles, m. p. 175—177°, is the main dinitration product of aceto-*ar*-tetrahydro- β -naphthalide, and is also obtained by nitration of aceto-4-nitro-*ar*-tetrahydro- β -naphthalide. On hydrolysis, it yields 3:4-di-nitro-*ar*-tetrahydro- β -naphthylamine, which melts at 157° and on reduction is converted into 1:2:3-triamino-*ar*-tetrahydronaphthalene.

ar-Tetrahydro-2:3-naphthylendiamine (for formation, see above) has m. p. 135—136° and b. p. 165°/13 mm. Its hydrochloride crystallises in glistening leaflets. With acetic acid it forms 2-methyl- $\beta\beta$ -*ar*-tetrahydronaphthiminazole (m. p. 251—252°) and with phenanthraquinone 2:3-*ar*-tetrahydronaphthylphenanthrazine, $C_{16}H_8 \begin{smallmatrix} \diagup N:C_6H_4 \\ \diagdown N:C_6H_4 \end{smallmatrix}$ (m. p. 214—216°). Acetyl-*ar*-tetrahydro-1:2-naphthylendiamine, m. p. 149—151°, on acetylation yields the

diacetyl derivative, and on hydrolysis gives the free diamine, which forms a *phenanthrazine*, m. p. 222-9—230°.

ar-Tetrahydro-1:3-naphthylenediamine, prepared by reduction of the dinitro-compound, forms pearly leaflets, m. p. 84—85°, b. p. 199—202°/10 mm. Its 1-*acetyl* derivative, obtained from 3-nitro-aceto-*ar*-tetrahydro- α -naphthalide, has m. p. 173°, and its 3-*acetyl* derivative, prepared from aceto-4-nitro-*ar*-tetrahydro- β -naphthalide, has m. p. 110—111°. The *diacetyl* derivative, obtained by acetylation of any of the above three substances, forms small, filamental needles, m. p. 245—246°. The *monoacetyl* derivative of *ar*-tetrahydro-1:4-naphthylenediamine is prepared by reducing aceto-4-nitro-*ar*-tetrahydro- α -naphthalide, and has m. p. 154—156°.

1:2:3-*Triamino-ar-tetrahydronaphthalene*, which is produced by reduction of 3:4-dinitro- or 1:3-dinitro-*ar*-tetrahydro- β -naphthylamine, is unstable in air, but yields a crystalline *hydrochloride*, and a *triacetyl* derivative which forms microscopic, white needles, m. p. 285°. 1:2:4-*Triamino-ar-tetrahydronaphthalene* is obtained by reducing the 1:2:4-trinitro-compound or the 2:4-dinitro-1-amino-derivative (see above). This base is also unstable, but its *triacetyl* derivative forms small needles, m. p. 315°.

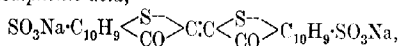
C. K. I.

Hydrogenated Naphthalenes and their Transformations.
III. Tetrahydronaphthalenesulphonic Acids, Tetrahydronaphthols, and their Derivatives. G. SCHROETER [with SVANOE, H. EINBECK, H. GELLER, and E. RIEBENSAMM] (*Annalen*, 1922, 426, 83—160).—Both *ar*-tetrahydronaphthalene-1-sulphonic acid, which has been prepared already by an indirect process by Morgan, Micklethwait, and Winfield (T., 1904, 85, 736), and *ar*-tetrahydronaphthalene-2-sulphonic acid (hitherto unknown) are obtained as their chlorides when chlorosulphonic acid is allowed to react with tetrahydronaphthalene. On the other hand, concentrated sulphuric acid gives chiefly the 2-sulphonic acid, 4—7% of the 1-sulphonic acid being produced simultaneously. Both sulphonic acids on fusion with alkalis yield the corresponding tetrahydronaphthols, and the sulphonyl chlorides on reduction give the tetrahydronaphthylthiols. The sulphonation of tetrahydronaphthalene, therefore, opens the way to the preparation of a large number of new aromatic compounds.

ar-Tetrahydronaphthalene-2-sulphonic acid separates with 2H₂O (m. p. 75°), its *sodium* salt with 1H₂O, and its *lead* salt with 1H₂O, which is given off at 130°. The *barium* and *ammonium* salts crystallise in the anhydrous condition in glistening leaflets. The acid *chloride*, m. p. 58°, b. p. 197—200°/18 mm., is obtained when phosphorus pentachloride acts on the acid, and on treatment with 10% ammonia passes into the *amide*, m. p. 133—137°. The *anilide*, prepared in similar manner, has m. p. 155—156°.

The mixtures obtained when chlorosulphonic acid is used for the sulphonation may be separated by crystallisation of the acids from chloroform, the 1-sulphonic acid separating first, or by pre-

precipitating the *lead* salt of *ar*-tetrahydronaphthalene-1-sulphonic acid by adding aqueous lead acetate to a concentrated solution of the acids, or by dissolving the sulphonamides in warm *N*-sodium hydroxide, from which the sodium salt of the 2-sulphonamide separates on cooling. The mixture of acid chlorides may also be reduced by means of zinc and hydrochloric acid to the *ar*-tetrahydronaphthylthiols, the sodium salts of which on condensation with sodium chloroacetate give the sodium salts of the *ar*-tetrahydronaphthylthiolacetic acids. The ammonium salt of the 2-compound is sparingly soluble and is precipitated if ammonium chloride is added. *ar*-Tetrahydronaphthyl-2-thiolacetic acid forms colourless needles, m. p. 78–80°; it may be prepared from pure *ar*-tetrahydronaphthalene-2-sulphonyl chloride. *ar*-Tetrahydronaphthalene-1-thiolacetic acid crystallises as glistening plates, m. p. 133–135°. *ar*-Tetrahydronaphthyl-2-thiolacetic acid forms a green solution in fuming sulphuric acid; on diluting, boiling, and making alkaline with sodium hydroxide, the sodium salt of bis-*ar*-tetrahydrothiophendisulphonic acid,



is precipitated.

When α -naphthol is reduced by means of two molecules of hydrogen at 200° in the presence of nickel, the product consists of about 10% of α -ketotetrahydronaphthalene, 25–30% of *ar*-tetrahydro- α -naphthol and a large quantity of tetrahydronaphthalene. At low temperatures, the ketone is the main product, and it seems probable that it forms an intermediate stage in the production of the hydrocarbon. On reduction by means of sodium and alcohol in moist ether, the ketone yields *ac*-tetrahydro- α -naphthol. *ac*-Tetrahydro- β -naphthol is the chief product of reduction (by the catalytic method) of β -naphthol.

ar-Tetrahydronaphthalene-2-sulphonic acid is therefore a valuable starting point in the preparation of *ar*-tetrahydro- β -naphthol and its derivatives. *ar*-Tetrahydro- β -naphthol forms a *methyl ether*, b. p. 129–131°/11 mm., prepared by the use of methyl sulphate, an *acetate*, b. p. 158°/14 mm., obtained using acetic anhydride, and a crystalline *benzoate*, prisms, m. p. 96°, b. p. 220–222°/10 mm., which is prepared by digesting the phenol with benzoyl chloride and pyridine. On sulphonation, *ar*-tetrahydro- β -naphthol-3-sulphonic acid is produced. It forms needles (2H₂O), m. p. 92°, yields a sparingly soluble *sodium* salt, and a *barium* salt (C₂₀H₂₂S₂O₆Ba), gives strongly coloured *azo-dyes* with the diazonium salts of *p*-nitro-aniline, sulphanilic acid, and naphthionic acid, and when heated with hydrochloric acid generates *ar*-tetrahydro- β -naphthol. 2-Methoxy-*ar*-tetrahydronaphthalene-3-sulphonic acid, m. p. 107°, is obtained by sulphonating the above-mentioned methyl ether. 1-Bromo-*ar*-tetrahydro- β -naphthol, m. p. 74°, may be prepared either by direct bromination of *ar*-tetrahydro- β -naphthol in carbon tetrachloride, or by desulphonation (using hydrochloric acid) of 1-bromo-*ar*-tetrahydro- β -naphthol-3-sulphonic acid (*sodium* salt, crystallises with 3H₂O) which is produced by sulphonation of 1-bromo-*ar*-tetrahydro-

β -naphthol, or, alternatively, by bromination of *ar*-tetrahydro- β -naphthol-3-sulphonic acid. On dibromination, *ar*-tetrahydro- β -naphthol yields 1:3-dibromo-*ar*-tetrahydro- β -naphthol, m. p. 37°; b. p. 198—201°/15 mm., which may also be prepared by the action of bromine on *ar*-tetrahydro- β -naphthol-3-sulphonic acid or on 1-bromo-*ar*-tetrahydro- β -naphthol-3-sulphonic acid, and is characterised by a well-crystallising acetate, m. p. 87°. 1-Bromo-3-nitro-*ar*-tetrahydro- β -naphthol, long, yellow needles, m. p. 129°, is obtained by treating 1-bromo-*ar*-tetrahydro- β -naphthol-3-sulphonic acid with nitric acid, the sulphonic acid group being replaced. The sodium salt forms red leaflets, and the methyl ether, obtained with the aid of methyl sulphate, yellow needles, m. p. 64°. 1-Chloro-3-nitro-*ar*-tetrahydro- β -naphthol, which forms yellow needles, m. p. 96°, is obtained by chlorinating *ar*-tetrahydro- β -naphthol-3-sulphonic acid and treating the crude product with nitric acid. On reduction by stannous chloride, 1-bromo-3-nitro-*ar*-tetrahydro- β -naphthol yields a mixture of 1-bromo-3-amino-*ar*-tetrahydro- β -naphthol, which melts at 127° and yields a hydrochloride, sulphate, and nitrate sparingly soluble in cold water, and 3-amino-*ar*-tetrahydro- β -naphthol, which crystallises in leaflets, m. p. 202°, and gives a hydrochloride and a nitrate easily soluble and a sulphate sparingly soluble in cold water. 1-Bromo-3-amino-2-methoxy-*ar*-tetrahydronaphthalene, the sulphate of which crystallises with 4H₂O, is obtained by reduction of the corresponding nitro-compound. 3-Amino-*ar*-tetrahydro- β -naphthol may also be prepared by hydrolysing its carbonyl derivative, C₁₀H₁₀ $\begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$ CO (below), m. p. 196°. The piperonyl

compound, C₁₀H₁₀ $\begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$ CH·C₆H₄·O₂CH₂, m. p. 160°, is obtained

from the amino-phenol and piperonal, and on methylation with methyl sulphate and alkalis yields 3-piperonylideneamino-2-methoxy-*ar*-tetrahydronaphthalene, OMe·C₁₀H₁₀·N·CH·C₆H₄·O₂CH₂, m. p. 126°, which when hydrolysed gives 3-amino-2-methoxy-*ar*-tetrahydronaphthalene, m. p. 86°. 1-Amino-*ar*-tetrahydro- β -naphthol is obtained by coupling *ar*-tetrahydro- β -naphthol with sulphanilic acid diazide or with benzenediazonium chloride and reducing the azo-compound. 1-Benzeneazo-*ar*-tetrahydro- β -naphthol, m. p. 84°, gives a monobromo-substitution product, m. p. 204°; 1-amino-*ar*-tetrahydro- β -naphthol forms colourless leaflets, m. p. 148°, and yields a crystalline hydrochloride and sulphate. An isomeric benzeneazo-*ar*-tetrahydro- β -naphthol, m. p. 110°, is occasionally also formed: on reduction, it yields 1-amino-*ar*-tetrahydro- β -naphthol, m. p. 173°, the sulphate of which separates from 2*N*-sulphuric acid. The carbonyl derivative, produced by heating with carbamide, forms small, red needles, m. p. 188°; it lowers the melting point, 189—190°, of the carbonyl derivative of 1-amino-*ar*-tetrahydro- β -naphthol, which is prepared in a similar manner. 1-Amino-2-methoxy-*ar*-tetrahydronaphthalene is produced by reducing 2-methoxy- α -naphthylamine (m. p. 54°, although 84° is the m. p. recorded in the literature) by means of sodium and amyl alcohol. It has m. p. 64°; b. p. 195—200°/20 mm., and on hydrolysis by means of hydro-

chloric acid at 180—190° yields 1-amino-*ar*-tetrahydro- β -naphthol. *Nitro-*ar*-tetrahydronaphthalene-3-sulphonic acid*, which may be prepared by directly sulphonating 1-nitro-*ar*-tetrahydronaphthalene, and is characterised by a crystalline *amide*, m. p. 189°, gives *ar-tetrahydro- α -naphthylamine-3-sulphonic acid* on reduction by means of stannous chloride or by iron and hydrochloric acid, but the amino-acid is not converted into 4-amino-*ar*-tetrahydro- β -naphthol on fusion with alkalis. The main product is *ar-tetrahydro- α -naphthylamine*, which is also obtained when the amino-sulphonic acid is condensed with *p*-toluenesulphonyl chloride before fusing with alkalis. However, 4-acetylamino-*ar-tetrahydro- β -naphthol*, red needles, m. p. 222°, is readily produced by the diazo-reaction applied to 4-acetylamino-*ar-tetrahydro- β -naphthylamine* (1-acetyl-derivative of *ar-tetrahydro-1:3-naphthylenediamine*, preceding abstract), and on hydrolysis by means of fuming hydrochloric acid gives 4-amino-*ar-tetrahydro- β -naphthol*, leaflets, m. p. 177°, which is characterised by having a sparingly soluble *hydrochloride*. When the unseparated mixture of 1- and 2-nitro-*ar-tetrahydronaphthalene* is sulphonated there is produced, along with nitro-sulphonic acid described above, an isomeride having a much more soluble sodium salt and consisting in all probability of 2-nitro-*ar-tetrahydronaphthalene-4-sulphonic acid*. It forms an *amide*, m. p. 211—212°, and on reduction yields *ar-tetrahydro- β -naphthylamine-4-sulphonic acid*, the *hydrochloride* of which is soluble in 120 parts of hot water. 1:3-Dinitro-*ar-tetrahydro- β -naphthol*, yellow needles, m. p. 141°, is produced by adding nitric acid (*d* 1.4) to a solution of *ar-tetrahydro- β -naphthol* in sulphuric acid. Its salts are for the most part sparingly soluble in water, the sodium, potassium, ammonium, barium, and lead salts being easily precipitated. The dry sodium salt on heating with methyl sulphate in toluene yields 1:3-dinitro-2-methoxy-*ar-tetrahydronaphthalene*, which forms colourless needles, m. p. 86.5°. On reduction by means of ethereal stannous chloride, 1:3-dinitro-*ar-tetrahydro- β -naphthol* yields 1-nitro-3-amino-*ar-tetrahydro- β -naphthol*, copper-coloured needles, m. p. 127°, and in a similar way the nitro-methoxy-compound gives 1-nitro-3-amino-2-methoxy-*ar-tetrahydronaphthalene*, which has m. p. 117°, and forms a sparingly soluble *hydrochloride*. 1:3-Diamino-*ar-tetrahydro- β -naphthol*, leaflets, m. p. 214—216°, is obtained when the dinitro-compound is reduced by alcoholic stannous chloride, and 1:3-diamino-2-methoxy-*ar-tetrahydronaphthalene*, prisms, m. p. 89°, when the dinitro-methoxy-derivative is treated similarly or reduced catalytically; its *hydrochloride* is obtained as a colourless, crystalline precipitate with the aid of ethereal hydrogen chloride. When *ar-tetrahydro- β -naphthol* is heated under pressure with carbon dioxide in the presence of alkalis, 2-hydroxy-*ar-tetrahydronaphthalene-3-carboxylic acid*, m. p. 182°, is produced. Its sodium salt crystallises without water of crystallisation and its calcium salt is sparingly soluble. The methyl ester, obtained by direct esterification, has m. p. 42°, b. p. 179°/15 mm., and forms a sparingly soluble sodium compound, $\text{ONa}\cdot\text{C}_{10}\text{H}_{10}\text{CO}_2\text{Me}$; the ethyl ester is a liquid, b. p. 179°/13 mm. Hydrazine converts

the methyl ester into a *hydrazide*, $\text{OH}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}\cdot\text{N}_2\text{H}_5$, m. p. 146° , which readily condenses with acetone, forming an *isopropylidene hydrazone*, $\text{HO}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}_2$, m. p. 235° , and on treatment with nitrous acid yields an *azide*, $\text{HO}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}\cdot\text{N}_3$, m. p. $99-100^\circ$, which on heating eliminates nitrogen and gives the carbonyl derivative of *ar-tetrahydro-2:3-naphthylenediamine* mentioned above. The hydroxy-acid also yields an *anilide*, m. p. $182-184^\circ$, an *acetyl* derivative, $\text{OAc}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}_2\text{H}$, m. p. $142-143^\circ$, and a nitro-derivative, *1-nitro-2-hydroxy-ar-tetrahydronaphthalene-3-carboxylic acid*, m. p. $200-202^\circ$, which on catalytic reduction gives *1-amino-2-hydroxy-ar-tetrahydronaphthalene-3-carboxylic acid*. The latter has m. p. $208-210^\circ$, and is characterised by a sparingly soluble *hydrochloride*, and by a *diacetyl* derivative, $\text{NHAc}\cdot\text{C}_{10}\text{H}_9(\text{CO}_2\text{H})\cdot\text{OAc}$, m. p. $180-181^\circ$, which is prepared by acetylating with acetic anhydride in the presence of a trace of sulphuric acid.

4-Amino-ar-tetrahydro- α -naphthol may be obtained by reduction (using stannous chloride) of *4-nitroso-ar-tetrahydro- α -naphthol* (m. p. $161-163^\circ$) which Green and Rowe (T., 1918, **113**, 955) erroneously supposed to be *4-nitro-ar-tetrahydro- α -naphthol*, or by coupling *ar-tetrahydro- α -naphthol* with sulphanilic acid diazide and reducing the *ar-tetrahydro- β -naphthol-4-azobenzene-*p*-sulphonic acid* so obtained by means of alkaline hyposulphite. The base has m. p. 146.8° and b. p. $208-210^\circ/10$ mm. The ethyl ether ("*p*-amino-*ar-tetrahydronaphthyl* ethyl ether," Jacobsen and Turnbull, A., 1898, i, 441) may be obtained by ethylating *4-benzene-azo-ar-tetrahydro- α -naphthol* with ethyl bromide and alcoholic potassium hydroxide and reducing the product catalytically in the presence of nickel. *2-Amino-ar-tetrahydro- α -naphthol*, m. p. $110-111^\circ$, is readily obtained by reducing Green and Rowe's *2-nitro-ar-tetrahydro- α -naphthol* (*loc. cit.*); its *hydrochloride*, on heating with carbamide, yields a *carbonyl* derivative, $\text{C}_{10}\text{H}_{10}\langle\begin{smallmatrix} \text{NH} \\ \text{O} \end{smallmatrix}\rangle\text{CO}$, m. p. 205° , which is also produced when *ar-tetrahydro- α -naphthol-2-carboxylazide* (see below) is heated in toluene. *3-Acetyl-amino-ar-tetrahydro- α -naphthol*, colourless needles, m. p. 211° , is prepared by hydrolysis of the diazonium salt obtained from *3-acetyl-amino-ar-tetrahydro- α -naphthylamine* (3-acetyl derivative of *ar-tetrahydro-1:3-naphthylenediamine*, preceding abstract). On hydrolysis with fuming hydrochloric acid, it yields *3-amino-ar-tetrahydro- α -naphthol* which forms leaflets, m. p. 197° , and gives a *hydrochloride* crystallising in colourless needles. *1-Hydroxy-ar-tetrahydronaphthalene-2-carboxylic acid*, m. p. $165-166^\circ$, is obtained by the action of carbon dioxide under pressure on *ar-tetrahydro- α -naphthol* in the presence of alkalis. The sodium salt, $\text{OH}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}_2\text{Na}\cdot 3\text{H}_2\text{O}$, crystallises in leaflets. The *acetyl* derivative, $\text{OAc}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}_2\text{H}$, obtained with the aid of acetic anhydride, has m. p. 170° ; the *methyl* ester, $\text{OH}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}_2\text{Me}$, m. p. 36° , b. p. $190^\circ/16$ mm.; the *hydrazide*, $\text{OH}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}\cdot\text{N}_2\text{H}_5$, m. p. 205° ; the *isopropylidenehydrazone*, $\text{OH}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}_2$, m. p. 136° ; and the *azide*, $\text{OH}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}\cdot\text{N}_3$, m. p. 84° , are prepared like the isomerides previously mentioned.

C. K. I.

Influence of Substitution in the Components on Equilibria in Binary Solutions. XXXIV. The Binary Systems of Anthracene with Nitro-derivatives of Benzene. ROBERT KREMANN and ROBERT MÜLLER II (*Monatsh.*, 1921, **42**, 181—197; cf. following abstract).—In the order of diminishing affinity towards nitro-compounds, the hydrocarbons as yet investigated may be arranged in the following order: naphthalene, acenaphthene, phenanthrene, and benzene, fluorene, triphenylmethane, and diphenylmethane. Examination of the binary systems formed by anthracene with nitro-derivatives of benzene and phenol show that anthracene occupies a position in the above series immediately before tri- and di-phenylmethanes.

The positions and percentages of anthracene corresponding with the eutectics formed by the binary systems of anthracene with nitrobenzenes are: *o*-dinitrobenzene, 110°, 12.5%; *m*-dinitrobenzene, 84°, 8%; *p*-dinitrobenzene, 146°, 35%; 2:4-dinitrotoluene, 66°, 9%; 2:4:6-trinitrotoluene, 75°, 6%. The system anthracene-1:3:5-trinitrobenzene forms a compound (1 mol.:1 mol.), m. p. 165°, which gives a eutectic with trinitrobenzene at 112° containing 4%, and a eutectic with anthracene at 162° containing 51% of anthracene.

With *o*-(*p*)-nitrophenol, anthracene gives a eutectic at 44° (106°) containing 2% (6%) of anthracene. With *m*-nitrophenol, a compound (1 mol.:1 mol.) is formed, m. p. 187°, this giving with anthracene at 186° a eutectic containing 59%, and with *m*-nitrophenol at 93° a eutectic containing 3% of anthracene. The system anthracene-2:4-dinitrophenol forms a eutectic at 101°, containing 15.5% of anthracene.

T. H. P.

Influence of Substitution in the Components on Equilibria in Binary Solutions. XXXI. The Binary Systems of Triphenylmethane with Amines and Phenols. ROBERT KREMANN, FRIEDRICH ODELGA, and OTTMAR ZAWODSKY (*Monatsh.*, 1921, **42**, 117—145; cf. Kremann and Wlk, A., 1919, ii, 458).—The binary systems formed by triphenylmethane with *p*-toluidine, α - and β -naphthylamines, and *m*- and *p*-phenylenediamines exhibit only simple eutectics. With *m*-phenylenediamine, two liquid layers are formed in the region corresponding with 20—91% of triphenylmethane, the temperature of the non-variant equilibrium in this region during the crystallisation of triphenylmethane being 81°. Thus, of the amines examined, only aniline gives a compound with triphenylmethane; for this system the authors find the maximum temperature 67.5° and for the eutectic between triphenylmethane and the compound, 67° and 72% of triphenylmethane, whereas Hartley and Thomas (T., 1906, **89**, 1024) found 71.6°, 76°, and 71.5% of triphenylmethane respectively. The total affinity between triphenylmethane and aniline is undoubtedly slight and is annulled by the least alteration in the molecular character of the amine.

Like diphenylmethane, triphenylmethane, forms no compounds with phenol, α - and β -naphthols, the three dihydroxybenzenes,

pyrogallol, the three nitrophenols, and picric acid. Somewhat extensive miscibility gaps in the liquid condition occur in the binary systems formed by triphenylmethane with resorcinol, quinol, pyrogallol, and picric acid, and in some cases solid solutions appear to be formed between triphenylmethane and phenols.

The positions of the eutectics in the binary systems formed by triphenylmethane with *p*-toluidine, α - and β -naphthylamines, and *p*- and *m*-phenylenediamines correspond respectively with the following temperatures and percentages of triphenylmethane: 33°, 36%; 37°, 33%; 72°, 75%; 87.5°, 97%; 60°, 3%.

The corresponding results for the binary systems formed by triphenylmethane with phenols are: Phenol, 31°, 26%; β -naphthol, 77°, 80%; α -naphthol, 74°, 70%; catechol, 80°, 82%; resorcinol, 87°, 94%; quinol, 91°, about 100%; pyrogallol, 89°, 97.5%; *o*-nitrophenol, 36°, 30%; *m*-nitrophenol, 80°, 76%; *p*-nitrophenol, 86°, 92.5%. In some cases, it cannot be decided whether the pure components or saturated mixed crystals of the solid solutions of the two components take part in the eutectic. The latter is probable in the systems containing the two naphthols, since mixtures at some distance from the eutectic solidify at temperatures higher than the eutectic temperature. In the systems containing triphenylmethane and *m*-(*p*-)nitrophenol, thermal effects occur below the eutectic temperatures, namely, at 75° (91°); for these no explanation is advanced.

T. H. P.

Preparation of Dihydroxyperylene. ALOIS ZINKE (Brit. Pat. 165771).—One part of 2:2'-dimethoxy-1:1'-dinaphthyl or other alkyl derivative of dihydroxydinaphthyl is heated with 4 parts of aluminium chloride with exclusion of moisture for two hours at 140–150°. The molten mass is treated with hydrochloric acid and the dihydroxyperylene formed is separated and purified by reprecipitation from sodium hydroxide solution or glacial acetic acid, in which reagents it is readily soluble with an intense green fluorescence. 1:12-Dihydroxyperylene is also readily soluble in benzene and toluene, but sparingly so in alcohol. Its solution in aqueous sodium hydroxide is readily oxidisable to the quinone, which, however, is again reduced on treatment with sodium hyposulphite.

G. F. M.

Preparation of Perylene. ALOIS ZINKE (Brit. Pat. 165770).—1:12-Dihydroxyperylene (cf. preceding abstract) is reduced by distilling with or over zinc dust or iron powder. For example, perylene is obtained as a reddish-yellow oil which, after solidification, is purified by crystallisation, by distilling a mixture of 1 part of dihydroxyperylene and 2 parts of zinc dust in a current of hydrogen and passing the vapours over heated pumice stone impregnated with zinc.

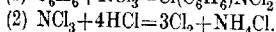
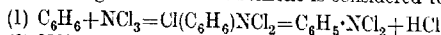
G. F. M.

The Reaction between Sulphur Monochloride and Aniline. S. COFFEY (*Rec. trav. chim.*, 1921, 40, 747–752; cf. Michaelis, A., 1891, 74, 310 and 715).—In attempting to prepare the sulphur

analogue of nitrobenzene by the action of sulphur monochloride on aniline in dilute ethereal solution, quantitative reaction takes place according to the equation $3\text{NH}_2\text{Ph} + \text{S}_2\text{Cl}_2 \rightarrow \text{NPhS}_2 + 2\text{NH}_3\text{PhCl}$, provided the temperature is sufficiently low. The compound NPhS_2 is a thick, red liquid which cannot be distilled or crystallised. Some of its chemical properties are described. The name dithio-phenylamine is suggested in place of thionitrobenzene, as the substance is analogous to the thionylamines. The nitrogen-sulphur linking is very unstable.

H. J. E.

Chlorination and the Formation of Chloroamines by means of Nitrogen Trichloride. GEORGE H. COLEMAN and WILLIAM ALBERT NOYES (*J. Amer. Chem. Soc.*, 1921, 43, 2211—2217).—Nitrogen trichloride reacts with ethyl chloride, giving, among other products, ethylene chloride, which is not a normal product of the action of free chlorine on ethyl chloride in the absence of a catalytic agent. With toluene, nitrogen chloride gives benzyl chloride and the monochlorotoluenes, together with more highly chlorinated derivatives. With benzene, the main product is benzene hexachloride. In addition to the above products, toluene, benzene, and benzyl chloride all give with nitrogen trichloride small amounts of *N*-chloroamines, the chloroamine group being located in the nucleus in each case, and not in the side chain. These chloroamines are then further chlorinated by the nitrogen trichloride or free chlorine. Thus with benzene the ultimate product is probably pentachlorophenyldichloroamine, $\text{C}_6\text{Cl}_5\cdot\text{NCl}_2$. These chlorinations take place at the ordinary temperature, and hence are not molecular rearrangements, but similar to the chlorination of aniline hydrochloride by free chlorine. The chlorophenyldichloroamine is decomposed by hydrochloric acid, giving chlorine and chloroaniline. The action of nitrogen chloride on benzene is considered to be



The free chlorine from the second reaction chlorinates the chloroamine. The formation of hydrogen chloride in reaction (1) involves a change of positive chlorine to negative, and this possibly accounts for the formation of considerable quantities of free nitrogen.

W. G.

Hydroxybenzyldimethylamine. A. MADINAVEITIA (*Anal. Fis. Quím.*, 1921, 19, 259—264).—Following the method indicated in Bayer's patent (D.R.-P. 92309), *o*-hydroxybenzyldimethylamine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NMe}_2$, was prepared by the action of 40% formaldehyde on a mixture of phenol and aqueous dimethylamine. The reaction is incomplete in the cold, but is completed by boiling for three to four hours under a reflux condenser. On cooling, the mixture is acidified with hydrochloric acid and extracted with ether to remove excess of phenol. Excess of aqueous ammonia is added and the amine thus liberated is extracted with ether. The ethereal solution is dried with anhydrous sodium sulphate, and after removal of the ether by evaporation the residue is fractionated.

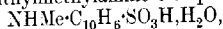
The base thus obtained has b. p. 105—106°/18 mm.; n_D^{25} 1.5273. The *picrate* crystallises in rosettes, m. p. 151°. By treatment of the base with acetic anhydride and saponification of the acetate, saliretin is obtained. By a similar reaction, using guaiacol, a

compound of formula $\text{OH} \begin{array}{c} \text{OMe} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_3 \end{array} \text{CH}_2\text{NMe}_2$ is obtained; it is an oil with b. p. 147—148°/15 mm.; the *picrate* has m. p. 202°. By hydrolysis of the diacetate, vanillyl alcohol is obtained (cf. Tiffeneau, A., 1911, i, 778, 810). G. W. R.

Derivatives of 2:4:6-Trinitrobenzaldehyde. II. ALEXANDER LOWY and WILMER BALDWIN (*J. Amer. Chem. Soc.*, 1921, 43, 1961—1963).—A continuation of previous work (cf. Lowy and Balz, A., 1921, i, 337). The following compounds are described: 2:4:6-Trinitrobenzylidene-*o*-phenetidine, m. p. 178.5°; 2:4:6-trinitrobenzylidene-*p*-phenetidine, m. p. 177°; 2:4:6-trinitrobenzylidene-*o*-anisidine, m. p. 171.5°; 2:4:6-trinitrobenzylidene-*p*-anisidine, m. p. 182°; 2:4:6-trinitrobenzylidene-*o*-chloroaniline, m. p. 187°; 2:4:6-trinitrobenzylidene-*p*-chloroaniline, m. p. 180°; and 2:4:6-trinitrobenzylidene-2:4-dichloroaniline, m. p. 198°.

When the condensations of 2:4:6-trinitrobenzaldehyde with *o*-chloroaniline, *p*-chloroaniline, and 2:4-dichloroaniline were carried out in hot glacial acetic acid solution, products were obtained having m. p. in all cases approximately 100° higher than those of the products prepared in the cold solution. These compounds are probably bimolecular condensation products. W. G.

β -Naphthylmethylamine-6-sulphonic Acid. GILBERT T. MORGAN and HORACE SAMUEL ROOKE (*J. Soc. Chem. Ind.*, 1920, 41, 1—37).— β -Naphthylmethylamine-6-sulphonic acid,



colourless crystals, m. p. 292°, after becoming changed at 280°, is obtained by the action of methylamine hydrochloride and aqueous sodium hydroxide on Schäffer salt at 180—200°. The following salts are described: sodium (+3H₂O and anhydrous), potassium (+3H₂O and anhydrous), calcium (+6H₂O and anhydrous), barium (+10H₂O and anhydrous), zinc (+6H₂O and anhydrous), magnesium (+6H₂O and anhydrous), copper, silver, and lead. The dyes produced by coupling β -naphthylmethylamine-6-sulphonic acid with the diazo-derivatives from aniline, *p*-nitroaniline, picramic acid, diaminstilbenedisulphonic acid, and tolidine are described: sodium benzeneazo- β -naphthylmethylamine-6-sulphonate forms bright red crystals. β -Naphthylmethylnitrosoamine-6-sulphonic acid, SO₃H·C₁₀H₆·NMe·NO, yellow needles, is converted by alcoholic hydrogen chloride into 1-nitroso- β -naphthylmethylamine-6-sulphonic acid, orange crystals. The latter substance is converted by evaporation to dryness of its solution in hydrochloric acid or by treatment with acetic acid and zinc chloride into $\alpha\beta$ -naphthiminazole-6-sulphonic acid, SO₃H·C₁₀H₆· $\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{CH} \end{array}$, pale yellow needles. Acetyl- β -naphthylmethylamine-6-sulphonyl chloride, NMeAc·C₁₀H₆·SO₂Cl,

crystallises in prismatic needles, m. p. 142—143°; it is converted by ethyl alcohol into the corresponding *ethyl ester*, colourless needles, m. p. 125—126°, and by ammonia into the *sulphonamide*, colourless, prismatic needles, m. p. 184—185°. *Benzoyl-β-naphthylmethylamine-6-sulphonyl chloride* forms colourless, rhomboidal prisms, m. p. 115—116°, and the corresponding *sulphonamide* crystallises in brownish-white plates, m. p. 225—226°. Sodium β-naphthylmethylamine-6-sulphonate is transformed by methyl sulphate in alkaline solution into the quaternary ammonium salt, $\text{SO}_3\text{Na}\cdot\text{C}_{10}\text{H}_6\cdot\text{NMe}_3\cdot\text{SO}_4\text{Me}\cdot 4\text{H}_2\text{O}$, which is converted by concentrated aqueous potassium hydroxide solution into *potassium β-naphthyltrimethylamine-6-sulphonate*, $\text{SO}_3\text{K}\cdot\text{C}_{10}\text{H}_6\cdot\text{NMe}_3\cdot 3\text{H}_2\text{O}$.

H. W.

Freezing-point Diagram of the System Phenol-Water. F. H. RHODES and A. L. MARKLEY (*J. Physical Chem.*, 1921, 25, 527—534).—The complete freezing-point diagram of the system phenol-water has been experimentally determined. It is shown that pure phenol has a melting point of 40·8°, a value which is considerably lower than the usually accepted value of 42—43°. Phenol forms a definite hydrate, $2\text{PhOH}\cdot\text{H}_2\text{O}$, m. p. 15·9°. The system consists of stable equilibria between phenol, phenol hydrate, and water, and metastable equilibria between anhydrous phenol and water. Because of the tendency toward suspended transformation, the solid phase which ordinarily appears when a mixture of phenol and water is cooled is the metastable anhydrous phenol. Hydrated crystals were obtained only by seeding with the hydrate or by cooling to very low temperatures. Phenol hydrate forms a eutectic with water containing 95% water at 0·85° and one with phenol containing 8·25% of water at 15·8°. In the metastable region at 1·7°, two liquid phases appear, a saturated solution of phenol in water and a saturated solution of water in phenol.

J. F. S.

The Action of Nitrous Acid on Phenols. H. A. J. SCHOUTSEN (*Rec. trav. chim.*, 1921, 40, 753—762; cf. Nietzki, A., 1890, 56).—By a modification of Liebermann's reaction, indophenols may be prepared from phenols in one operation. The reaction takes place in two stages, first the formation of a nitroso-compound, followed by the condensation of this compound with a second molecule of the phenol. The facility with which the second stage takes place depends on the nature of the intermediate nitroso-phenol. The colouring matters formed in these reactions should be classed among the indophenols as only a small proportion is transformed into oxazine derivatives by the closing of the ring. The author criticises the views put forward by Meyer and Elbers A., 1921, i, 240).

H. J. E.

Metallic Derivatives of Nitrophenolic Compounds. III. Nitrophenoxides of the Alkali Metals. DOROTHY GODDARD and ARCHIBALD EDWIN GODDARD (T., 1922, 121, 54—58).

Compound Formation in Phenol-Cresol Mixtures. JAMES KENDALL and J. J. BEAVER (*J. Amer. Chem. Soc.*, 1921, **43**, 1853—1687; cf. this vol., ii, 32, 33).—Phenol and the three cresols have been exhaustively purified by repeated fractionation and absolute purity determined by a minimum specific conductivity. The following data are recorded for the pure substances: Phenol, freezing point $39.70 \pm 0.02^\circ$, specific conductivity 40° , 11.98×10^{-8} and 50° , 14.07×10^{-8} ; *o*-cresol, f. p. $30.60 \pm 0.02^\circ$, specific conductivity 0.127×10^{-8} at 25° ; *p*-cresol, f. p. $34.55 \pm 0.02^\circ$, specific conductivity 1.378×10^{-8} at 25° ; *m*-cresol, f. p. 11.10 ± 0.02 , specific conductivity 1.397×10^{-8} at 25° . These values are compared with the best existing data. The specific conductivity of the six possible binary systems made up from phenol and the cresols has been determined for the whole range of concentrations at 25° . A series of viscosity determinations of these same binary systems is recorded for 25° . A series of molecular weight determinations of the pure substances and certain of the mixtures in solutions in benzene have been made by the freezing-point method. The results indicate that without exception no increase in molecular complexity occurs on mixing these substances. This is in complete accordance with the views correlating additive compound formation with diversity in character of the components, put forward previously (*loc. cit.*). It is apparently in disagreement, however, with the fact that Dawson and Mountford (T., 1918, **113**, 923) succeeded in isolating definite compounds from cresol-phenol mixtures in five out of the six systems. It is, however, shown that the compounds obtained by these authors are to be regarded as substitution rather than as additive compounds. Under this view, no conflict exists between the results of Dawson and Mountford and those of the present work; both fall directly into line with the general theory.

J. F. S.

Catalytic Hydrogenation of Polyphenols by the Wet Way. J. B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1921, **173**, 1365—1367).—Quinol, resorcinol, catechol, pyrogallol, phloroglucinol, and hydroxyquinol can be reduced in alcohol by the action of hydrogen under a pressure of 30—50 kilos. in the presence of reduced nickel at 115 — 130° or in aqueous solution at slightly higher temperatures. At higher temperatures, secondary reactions occur. At 130° in alcoholic solution, resorcinol gives cyclohexane-1:3-diol, but at 180° cyclohexanol is the principal product.

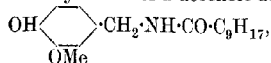
W. G.

Waage's Phytochemical Synthesis of Phloroglucinol from Dextrose. M. NIERENSTEIN (*Nature*, 1920, **105**, 391).—A series of nearly eighty experiments, performed during fifteen years failed to confirm statements based on Waage's observations (A. 1891, 605; *Ber. deut. bot. Ges.*, 1890, **8**, 250), that phloroglucinol is formed when leaves floating in solutions of sugar are exposed to sunlight.

A. A. E.

Natural and Artificial Pepper-substances and the Relation between Chemical Constitution and Peppery Taste. ERWIN ORT and KURT ZIMMERMANN (*Annalen*, 1921, 425, 314–337).—The elucidation of the constitution of capsaicin by Nelson (A., 1919, i, 543) is made the basis of an examination of the extent to which the various features of the molecule contribute to produce the peppery taste characteristic of that substance.

Capsaicin is the vanillylamide of a decenoic acid,



and it is known that the vanillylamide of Δ^8 -undecenoic acid has a similar and about equally sharp taste. Undecenoic acid is, therefore, condensed with a number of bases more or less closely related to vanillylamine, and it is shown that the *p*-hydroxybenzylamide (m. p. 86°) has a taste considerably weaker than that of capsaicin, whilst the taste of the *o*-hydroxybenzylamide (not purified) is weaker still. Hence the presence of the methoxy-group and the particular orientation of the hydroxyl group in capsaicin both contribute to its taste. The presence of a phenolic hydroxyl group appears to be essential, since both the *anisylamide* (white leaflets, m. p. 91°) and the *benzylamide* (m. p. 51–52°) are tasteless. So also is the *p*-hydroxyphenylamide (m. p. 107°), which shows that the component amine must be of aliphatic type.

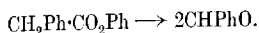
With regard to the conditions governing the character of the acid residu, it is found that the *vanillylamides* of Δ^8 -nonenoic acid, decenoic acid, and Δ^8 -undecenoic acid, have tastes of a comparable strength, whilst those of Δ^2 -heptenoic acid and *crotonic acid* possess much less pungent tastes. The taste of the *vanillylamide* of *cinnamic acid* (white powder, m. p. 138°) was also only feebly peppery, whilst that of the *vanillylamide* of *oleic acid* was exceedingly pungent but of different quality from the tastes of capsaicin and its closer homologues. On the other hand, the *p*-hydroxybenzylamide of Δ^8 -nonenoic acid tastes more strongly peppery than the corresponding amide of undecenoic acid (see above). These facts show (a) that the positions of the double bond in the acid residue has comparatively little influence on the peppery taste of the capsaicin-like amides, (b) that, on the other hand, the length of the carbon chain is important, acids with nine, ten, or eleven carbon atoms showing the phenomenon in the most marked and characteristic manner.

One of the most remarkable facts which emerged from the investigation is the necessity for an unsaturated linking in the acid component. The *vanillylamide*, m. p. 86°, of highly purified *stearic acid* is quite without taste, both in the solid state and in concentrated alcoholic solution. Commercially "pure" *palmitic acid*, on the other hand, gives a *vanillylamide* (m. p. 79°) which has a sharp taste, but this is due to the presence of traces of the *oleic acid* derivative. When the amide is purified by crystallisation from ether, the taste of the solid amide vanishes, but it is still

intense in alcoholic solution. A very delicate test for unsaturated acids may be based on these results.

The *piperidine* of *sorbic acid*, m. p. 77° , has a taste which is very bitter but not at all peppery. C. K. I.

Benzyl Compounds [Benzyl Alcohol]. J. MESSNER (*Pharm. Zentralh.*, 1922, **63**, 1).—The instability of aqueous solutions of benzyl alcohol, even in the absence of air, as, for example, when sealed up in ampoules, is ascribed to autoxidation, catalysed possibly by traces of alkali from the glass, resulting in the formation of 1 mol. of toluene, and 1 mol. of benzaldehyde and water from 2 mols. of the alcohol. A similar change occurs with aqueous solutions of benzyl benzoate, which after a week or so acquire a strong odour of benzaldehyde, remaining, however, neutral in reaction. In this case 2 mols. of benzaldehyde are formed by autoxidation of the ester according to the scheme:



G. F. M.

Influence of Substitution in the Components on Equilibria in Binary Solutions. XXXV. The Binary Systems of Triphenylcarbinol with Pyrogallol, Nitrophenols, Polynitrobenzenes, and Phenylenediamines. ROBERT KREMANN, HEINZ HOHL, and ROBERT MÜLLER II (*Monatsh.*, 1921, **42**, 199—220; cf. this vol., i, 131, 159).—Triphenylcarbinol (2 mols.) and pyrogallol (3 mols.) form a compound, m. p. 97° , giving at 65° a eutectic with triphenylcarbinol and at 76° a eutectic with pyrogallol, these containing respectively 70% and 49% of triphenylcarbinol. The latter forms with *o*- and *p*-nitrophenols eutectics at 41° and 97° containing 90% and 63% of the nitrophenol. Triphenylcarbinol and *m*-nitrophenol form a compound which appears to contain 1 molecule of the former and 2 molecules of the latter component, and undergoes considerable dissociation when fused. The system triphenylcarbinol-picric acid forms a compound (1 mol.: 1 mol.), m. p. 138.5° , which gives with picric acid at 110° a eutectic containing 23%, and with triphenylcarbinol at 122° a eutectic containing 67% of triphenylcarbinol.

The binary systems formed by triphenylcarbinol with *o*-, *m*-, and *p*-dinitrobenzenes, 2:4-dinitrotoluene, and 2:4:6-trinitrotoluene form eutectics at 102° , 82° , 132° , 65° , and 76° , respectively, corresponding with 67%, 82%, 64%, 88%, and 92% of the respective nitro-components. The system triphenylcarbinol-trinitrobenzene forms a compound, m. p. 134.5° , which contains 2 mols. of the alcohol to 3 mols. of the nitro-compound and gives eutectics with the components at 133° and 112° respectively and corresponding with 48% and 15% of triphenylcarbinol.

With the binary systems formed by triphenylcarbinol with *p*- and *m*-phenylenediamines, the fusion curves of the components meet in eutectic points at 118° and 59.5° respectively, these corresponding with 67% and 10% of triphenylcarbinol. T. H. P.

The Interaction of Aromatic Disulphides and Sulphuric Acid. SAMUEL SMILES and ERNEST WILSON McCLELLAND (T., 1922, 121, 86—90).

Preparation and Properties of the Benzoehloroamides. GEORGE ROBERT ELLIOTT (T., 1922, 121, 202—209).

Steric Hindrance of the Sulpho-acid Group. C. F. VAN DUIN (*Rec. trav. chim.*, 1921, 40, 724—735).—In preparing the methyl esters of isomeric sulphobenzoic acids, the yield is much greater in the case of the ortho-acid, whilst in the saponification of these esters the SO_3Na -group in the ortho-position considerably retards the reaction. Anomalous results are given by o-sulphamino-benzoic acid. The conclusions drawn are consistent with those of Remsen and Reid (A., 1899, i, 507). H. J. E.

Azomethine Derivatives of the 2- and 4-Hydroxy- α -Naphthaldehydes. GILBERT T. MORGAN and HARRY GORDON REEVES (T., 1922, 121, 1—7).

Reduction of Naphthalene- and Naphthol-carboxylic Acids. HUGO WEIL and HERMANN OSTERMEIER (*Ber.*, 1921, 54, [B], 3217—3219).—It has been shown previously that salicylic acid is reduced by sodium amalgam in the presence of boric acid to salicylaldehyde in good yield (A., 1908, i, 800). The observations have now been extended to certain carboxylic acids of naphthalene and the naphthols. Under these conditions, α -naphthoic acid is almost unaffected, whereas β -naphthoic acid is partly converted into β -naphthaldehyde, m. p. $60.5-61^\circ$ (*phenylhydrazone*, colourless leaflets, m. p. $217-218^\circ$). 1-Naphthol-2-carboxylic acid gives the corresponding aldehyde, m. p. 59° , the yield being 57%, calculated on the reduced acid. 2-Naphthol-3-carboxylic acid is transformed into an aldehyde, $\text{C}_{11}\text{H}_{12}\text{O}$, b. p. $122^\circ/12$ mm. (*phenylhydrazone*, m. p. 97°). The substance behaves like an aliphatic aldehyde, being resinified by alkali and reducing ammoniacal silver solution, Fehling's solution, and potassium permanganate in cold solution; it appears to be tetrahydro- β -naphthaldehyde, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2-\text{CH}\cdot\text{CHO} \\ | \\ \text{CH}_2-\text{CH}_2 \end{smallmatrix}$. It gives a bisulphite compound which is freely soluble in water. H. W.

Carboxylic Acids of the Semibenzene Group. K. v. AUWERS and K. ZIEGLER (*Annalen*, 1921, 425, 280—294).—This communication shows that the types of transformation previously discussed (A., 1911, i, 298) have some degree of generality.

Ethyl α -4-hydroxy-1-methyl-1-dichloromethyl- $\Delta^{2,3}$ -cyclohexadiene-4-propionate, $\text{CO}_2\text{Et}\cdot\text{CHMe}\cdot\text{C}(\text{OH}) \begin{smallmatrix} \text{CH}\cdot\text{CH} \\ | \\ \text{CH}\cdot\text{CH} \end{smallmatrix} \text{Me}\cdot\text{CHCl}_2$, is obtained as a viscous, dark oil (impure) by the action of ethyl α -bromopropionate and zinc dust on 1-methyl-1-dichloromethylcyclohexadien-4-one, and on hydrolysis by means of cold alcoholic alkali yields the corresponding acid, which forms stout, white

crystals, m. p. 123° (decomp.). On shaking with formic acid, the ester of the hydroxy-acid is dehydrated, forming *ethyl α-1-methyl-1-dichloromethyl-Δ^{2:5}-cyclohexadien-Δ⁴-propionate* ($d_4^{17.6}$ 1.2033, d_4^{20} 1.201, $n_D^{17.6}$ 1.56017, $n_D^{17.6}$ 1.56682, n_D^{20} 1.5657), which on hydrolysis by means of alcoholic potassium hydroxide yields the free acid, a yellow, crystalline powder, m. p. 101—103°, and can be regenerated from the acid by treating its silver salt with ethyl iodide. On heating, the acid undergoes isomeric change with the formation of *ββ-dichloro-α-p-tolylisobutyric acid*, needles, m. p. 135—136°, which when treated with alkali is converted into *β-chloro-α-p-dimethylstyrene*.

1:3-Dimethyl-1-dichloromethylcyclohexadien-4-one on condensation with ethyl bromoacetate and zinc yields *ethyl α-1:3-dimethyl-1-dichloromethyl-Δ^{2:5}-cyclohexadien-Δ⁴-acetate* ($d_4^{17.6}$ 1.2026, d_4^{20} 1.200, $n_D^{17.6}$ 1.56219, $n_D^{17.6}$ 1.56898, n_D^{20} 1.5679). The free acid, m. p. 125—126°, on heating in petroleum, is converted into *ββ-dichloro-α-m-4-xylylpropionic acid*, m. p. 132—132.5°, which on hydrolysis by means of boiling sodium carbonate solution yields *β-chloro-2:4-dimethylstyrene*. This substance on oxidation in aqueous acetone by permanganate gave *2:4-dimethylbenzaldehyde*, which was identified as its semicarbazone.

Ethyl ββ-dichloro-α-m-4-xylylpropionate, b. p. 170—175°/16 mm., is best obtained by the action of heat on *ethyl α-1:3-dimethyl-1-dichloromethyl-Δ^{2:5}-cyclohexadien-Δ⁴-acetate*. On boiling with alcoholic alkali, it is converted into *β-chloro-2:4-dimethylatropic acid*, $C_6H_3Me_2C(CO_2H)CHCl$, which crystallises in stout tablets, m. p. 111°. C. K. I.

Friedel and Crafts' Reaction. The Preparation of 2-p-Toluylbenzoic Acid. T. C. McMULLEN (*J. Amer. Chem. Soc.*, 1921, 43, 1965).—In the preparation of 2-p-toluylbenzoic acid from toluene, phthalic anhydride, and aluminium chloride good yields of the acid were obtained using 20 grams of toluene, 5 grams of the anhydride, and 9 grams of the chloride. Increasing the amount of phthalic anhydride or introducing acetic anhydride reduced the yield of acid very considerably or prevented its formation, but resulted in good yields of ditolyl phthalide (cf. Rubidge and Qua, A., 1914, i, 539). W. G.

Friedel and Crafts' Reaction. The Carbomethoxybenzoyl Chlorides with Aromatic Hydrocarbons and Aluminium Chloride. MAURICE E. SMITH (*J. Amer. Chem. Soc.*, 1921, 43, 1920—1924).—The reaction of each of the carbomethoxybenzoyl chlorides with benzene, toluene, and *m*-xylene, respectively, in the presence of aluminium chloride has been studied. In each case the reaction with toluene takes place in the para-position to the methyl group and with *m*-xylene in the para-position to one of the methyl groups.

o-Carbomethoxybenzoyl chloride gave under these conditions with benzene after hydrolysis of the ester *o*-benzoylbenzoic acid; with toluene *p*-toluyl-*o*-benzoic acid, and with *m*-xylene 2:4-di-

methylbenzoyl-*o*-benzoic acid. *m*-Carbomethoxybenzoyl chloride gave with benzene *m*-benzoylbenzoic acid; with toluene *p*-toluoyl-*m*-benzoic acid, m. p. 172°, giving a silver salt and a methyl ester, m. p. 108°; and with *m*-xylene 2:4-dimethylbenzoyl-*m*-benzoic acid, m. p. 168°, giving a silver salt and a methyl ester, m. p. 73°. *p*-Carbomethoxybenzoyl chloride gave with benzene *p*-benzoylbenzoic acid; with toluene *p*-toluoyl-*p*-benzoic acid, and with *m*-xylene 2:4-dimethylbenzoyl-*p*-benzoic acid, m. p. 185°, giving a silver salt and a methyl ester, m. p. 59°.

*iso*Phthalic and terephthalic acids were readily obtained by the oxidation of commercial xylene with potassium permanganate in the presence of sodium hydroxide, the two acids being separated by means of the differing solubilities of their barium salts. W. G.

The Friedel and Crafts' Reaction. Bromophthalic Anhydrides, Benzene, and Aluminium Chloride. H. N. STEPHENS (*J. Amer. Chem. Soc.*, 1921, 43, 1950—1956).—The various *o*-benzoylbromobenzoic acids and the diphenylbromophthalides have been prepared and identified. 3-Bromophthalic acid was prepared most satisfactorily from 3-aminophthalic acid by the Sandmeyer reaction. Its anhydride when boiled with benzene and aluminium chloride for four hours gave 6-benzoyl-2-bromobenzoic acid, m. p. 231.5°, probably identical with the compound, m. p. 219—221°, described by Pechmann as *o*-bromobenzoylbenzoic acid (cf. *Ber.*, 1879, 12, 2126). Under similar conditions, 4-bromophthalic anhydride gave 2-benzoyl-4-bromobenzoic acid, m. p. 193°, and 6-benzoyl-3-bromobenzoic acid, m. p. 172.5° (cf. Kohler, *Heritage*, and Burnley, A., 1910, i, 562).

When 3-bromophthalic anhydride is boiled as above with aluminium chloride and benzene and then to the mixture acetic anhydride and more benzene are added and the boiling is continued, a compound, m. p. 148—150°, is obtained which is not, however, a diphenylbromophthalide. Under similar conditions, 4-bromophthalic anhydride gives a mixture of diphenyl-5-bromophthalide, m. p. 186°, and diphenyl-4-bromophthalide, m. p. 115—116°. Diphenyl-3-bromophthalide, m. p. 131°, was obtained from the mixed anhydride, m. p. 168.5°, of 6-benzoyl-2-bromobenzoic acid and acetic acid. The mixed anhydride, m. p. 83—87°, of 2-benzoyl-4-bromobenzoic acid and acetic acid, and the mixed anhydride of 6-benzoyl-3-bromobenzoic acid and acetic acid were also prepared. W. G.

A New Alkylamine and certain of its Derivatives. HANS DERSIN (*Ber.*, 1921, 54, [B], 3158—3162).—Gabriel and Ohle (A., 1917, i, 565) have described the preparation of amino-alcohols by the action of alkylene oxides on phthalimide and subsequent elimination of the acid group. Since, however, the alkylene oxides are generally prepared with considerable loss from the halogenhydrins, it appears more advantageous to cause the latter to react directly with potassium phthalimide. This method has been used already for the preparation of β -hydroxy-*n*-propylamine (Gabriel

and Ohle, A., 1917, i, 563) and two further examples of its employment are now given.

Hydroxyethylphthalimide, $C_8H_4O_2 \cdot N \cdot CH_2 \cdot CH_2 \cdot OH$, m. p. 88—89°, is obtained from potassium phthalimide and ethylene chlorohydrin.

*iso*Butylene chlorohydrin, prepared from chloroacetone or chloroacetic ester and magnesium methyl bromide (but not iodide), is converted by potassium phthalimide into α -phthalimino- β -hydroxy- β -methylpropane, $OH \cdot CMe_2 \cdot CH_2 \cdot N \cdot C_8H_4O_2$, slender, colourless needles or leaflets, m. p. 106—107°. The yield is not very satisfactory. Attempts to prepare the substance from Grignard's reagents and ethyl phthaliminoacetate, acetonylphthalimide, or phthalylglycyl chloride were, however, fruitless. The phthalyl derivative is hydrolysed by sulphuric acid to *isobutaldehyde* and α -amino- β -hydroxy- β -methylpropane, $OH \cdot CMe_2 \cdot CH_2 \cdot NH_2$; the *hydrochloride*, very hygroscopic, colourless needles, m. p. 70—72°. *platinichloride*, long, very hygroscopic, yellow needles, m. p. 172° (decomp.), *picrate*, large, prismatic crystals, m. p. 165—175°, according to the manner of heating, and *aurichloride*, long, yellow needles or prisms, of the latter are described. The base is converted by phenylthiocarbimide into *N-phenyl-N'-hydroxyisobutylthiocarbamide*, $NHPh \cdot CS \cdot NH \cdot C_4H_9 \cdot OH$, colourless needles or prisms, m. p. 136—137°, which is transformed by fuming hydrochloric acid at 100°

into the isomeric 2-anilino-5 : 5-dimethylthiazoline, $\begin{matrix} CMe_2 \cdot S \\ | \\ CH_2 \cdot N \end{matrix} > C \cdot NHPh$,

colourless prisms, m. p. 153—154°. β -Chloro- α -amino- β -methylpropane *hydrochloride*, lustrous needles, m. p. 183° (decomp.), is obtained together with the chlorohydrin, $OH \cdot CMe_2 \cdot CH_2Cl$, when the alkylamine hydrochloride is heated with saturated hydrochloric acid at 100°; the oily free base smells like glue, and yields a *picrate*, long needles or plates, m. p. 159°. Potassium thiocyanate converts the chloroalkylamine hydrochloride into 2-amino-5 : 5-dimethylthiazoline (*picrate*, m. p. 103—106°). With benzoyl chloride and sodium hydroxide, the hydrochloride gives β -chloro- α -benzamido- β -methylpropane, $CMe_2Cl \cdot CH_2 \cdot NHBz$, m. p. 97—98°, which is transformed by boiling water into 2-phenyl-5 : 5-dimethyloxazoline, a liquid which gives a *picrate*, needles, m. p. 198—199°. The *platinichloride* of the chloroamine, $CMe_2Cl \cdot CH_2 \cdot NH_2$, crystallises in six-sided prisms, m. p. 200°.

α -Phthalimino- β -hydroxy- β -methylpropane exchanges its hydroxyl-group readily for a halogen atom when warmed with halogen acids. It thus gives β -chloro- α -phthalimino- β -methylpropane, $CMe_2Cl \cdot CH_2 \cdot N \cdot C_8H_4O_2$, needles, m. p. 88—89°, the corresponding *iodo*-compound, prisms, m. p. 100—101°, and *bromo*-derivative, needles or leaflets, m. p. 97°. The latter can be converted by potassium hydroxide, acetic acid, and nitrous acid into the *nitroso*-compound, $C_6H_4 \begin{matrix} CO \cdot N(NO) \cdot CH_2 \\ | \\ CO \cdot O \end{matrix} - CMe_2$ needles or prisms, m. p. 154° (decomp.).

Attempts to cause trimethylethylenechlorohydrin, $OH \cdot CMe_2 \cdot CHMeCl$, to react with potassium phthalimide were unsuccessful. H. W.

Synthesis of Inactive Para- and Anti-hydroxyaspartic Acids (Aminomalic Acids) [Aminohydroxysuccinic Acids].

H. D. DAKIN (*J. Biol. Chem.*, 1921, **48**, 273—291).—Attempts to obtain *aminohydroxysuccinic acid*, $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, either synthetically or as a degradation product of proteins have not hitherto been successful, although its isolation has been incorrectly reported (Skraup, A., 1904, i, 539; Neuberg and Silbermann, A., 1905, i, 418; Lossen, A., 1906, 798). In view of its possible occurrence in proteins it was therefore prepared by heating chloromalic acid with 5 parts of concentrated aqueous ammonia for about ten hours in an autoclave immersed in a boiling water-bath. After removal of chlorine, it was isolated from the reaction product by means of its lead salt. The acid so obtained forms a syrup which is difficult to crystallise unless seeded, and consists of a mixture of two optically inactive isomerides. Separation of these was effected by fractional crystallisation from water. The less soluble isomeride, the *para-acid* forms small, opaque cubes, decomposes slowly when heated above 235° , and is converted by nitrous acid into racemic acid. The more soluble form, the *anti-acid*, forms hexagonal plates and thick prisms, and gives mesotartaric acid on similar treatment. With phenylcarbimide, *phenylhydantoin* derivatives are produced, the *para*-compound forming bunches of white needles, m. p. $201.5\text{--}202.5^\circ$, and the *anti*, nacreous plates, m. p. $196\text{--}198^\circ$. The various salts produced have the following composition: (Para), $(\text{C}_4\text{H}_5\text{O}_5\text{N})_2\text{Ca}\cdot 5\text{H}_2\text{O}$; $\text{C}_4\text{H}_5\text{O}_5\text{N}\cdot\text{Ca}\cdot\text{Aq}$; $(\text{C}_4\text{H}_5\text{O}_5\text{N})_2\text{Ba}\cdot 3\text{H}_2\text{O}$; $\text{C}_4\text{H}_5\text{O}_5\text{N}\cdot\text{Ba}$; $(\text{C}_4\text{H}_4\text{O}_5\text{N})_2\text{Cu}_3\cdot 8\text{H}_2\text{O}$; $(\text{C}_4\text{H}_4\text{O}_5\text{N})_2\text{Zn}_3\cdot 7\text{H}_2\text{O}$. (Anti), $(\text{C}_4\text{H}_5\text{O}_5\text{N})_2\text{Ca}\cdot 4\text{H}_2\text{O}$; $\text{C}_4\text{H}_5\text{O}_5\text{N}\cdot\text{Ca}\cdot 2\text{H}_2\text{O}$; $(\text{C}_4\text{H}_5\text{O}_5\text{N})_2\text{Ba}\cdot 3\text{H}_2\text{O}$; $\text{C}_4\text{H}_5\text{O}_5\text{N}\cdot\text{Ba}$; $(\text{C}_4\text{H}_4\text{O}_5\text{N})_2\text{Cu}_3\cdot 8\text{H}_2\text{O}$; $(\text{C}_4\text{H}_4\text{O}_5\text{N})_2\text{Zn}_3\cdot 7\text{H}_2\text{O}$.

By heating chloromalic acid with aniline, the *dianilide of anilino-hydroxysuccinic acid*, $\text{CO}(\text{NHPh})\cdot\text{CH}(\text{NHPh})\cdot\text{CH}(\text{OH})\cdot\text{CO}(\text{NHPh})$, nodular clumps of bright yellow needles softening above 200° and melting at $210\text{--}211^\circ$, and *anilino-hydroxysuccinic acid anil*,

$\text{PhN} \begin{array}{l} \diagup \text{CO}\cdot\text{CH}\cdot\text{NHPh} \\ \diagdown \text{CO}\cdot\text{CH}\cdot\text{OH} \end{array}$, bright yellow plates, m. p. $238\text{--}239^\circ$, were obtained.

E. S.

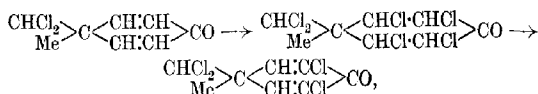
The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. II. Intramolecular Tautomerism. ERNEST HAROLD FARMER, CHRISTOPHER KELK INGOLD, and JOCELYN FIELD THORPE (*T.*, 1922, **121**, 128—159).

The Direct Acetalisation of Aldehydes. ROBERT DOWNS HAWORTH and ARTHUR LAPWORTH (*T.*, 1922, **121**, 76—85).

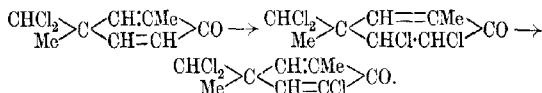
Catalytic Reduction of Nitrones. G. CUSMANO (*Gazzetta*, 1921, **51**, ii, 306—309).—Reduction of an aldonitrone, $\text{CHR}\cdot\text{NR}\cdot\text{O}$, by means of the Grignard reagent yields a β -hydroxylamine, $(\text{CH}_3\text{R})_2\text{NR}\cdot\text{OH}$ (Angeli, Alessandri, and Ajazzi-Mancini, A., 1911, i, 44), whereas the action of nascent hydrogen results in the formation of the Schiff's base, $\text{CHR}\cdot\text{NR}$. The author finds that catalytic

reduction by means of hydrogen in presence of platinum black converts aldo- and keto-nitrone almost quantitatively into β -substituted hydroxylamines, very small proportions of secondary amines being formed in addition. Thus, phenyl-*N*-phenylnitrone yields phenylbenzylhydroxylamine and benzyaniline, and the catalytic reduction of anisyl-*N*-phenylnitrone and diphenyl-*N*-phenylnitrone proceeds similarly. T. H. P.

Chloro- and Bromo-derivatives of Alkylated cycloHexa-dienones. K. VON AUWERS and K. ZIEGLER (*Annalen*, 1921, 425, 295—313).—It has been shown (A., 1911, i, 383) that the chlorination of 1-methyl-1-dichloromethylcyclohexadien-4-one takes the following course :



but that the presence of a methyl group in the "ortho"-position to the carbonyl group limits the additive power of the molecule :



In the present communication, it is shown (a) that a methyl group in the meta-position to the carbonyl group does not prevent the addition of the second two atoms of chlorine, but, nevertheless, retards it considerably, (b) that bromination is governed by the same rules as chlorination.

1 : 2-Dimethyl-1-dichloromethylcyclohexadien-4-one, when treated with chlorine in carbon disulphide, takes up two atoms of chlorine with the formation of 5 : 6-dichloro-1 : 2-dimethyl-1-dichloromethyl- Δ^2 -cyclohexen-4-one, which melts at 82—83° with evolution of gas, and, on treatment with potassium acetate in hot acetic acid solution, passes smoothly into 5-chloro-1 : 2-dimethyl-1-dichloromethyl- $\Delta^{2:3}$ -cyclohexadien-4-one. This substance forms small, stout prisms, m. p. 101—102°, and yields a *p*-nitrophenylhydrazone, m. p. 206—208°. When, however, the original ketone is treated in carbon tetrachloride solution with chlorine in sunlight, four atoms of chlorine are taken up, but the product is too unstable to admit of its being isolated, and passes under the conditions of its production into 3 : 5-dichloro-1 : 2-dimethyl-1-dichloromethyl- $\Delta^{2:3}$ -cyclohexadien-4-one, which forms glistening crystals, m. p. 87—90°, and shows no tendency to condense with *p*-nitrophenylhydrazine or to combine with chlorine.

Lack of tendency to combine with chlorine and *p*-nitrophenylhydrazine is also exhibited by 5-chloro-1 : 3-dimethyl-1-dichloromethyl- $\Delta^{2:3}$ -cyclohexadien-4-one, and is to be attributed to the presence of two substituents in positions adjacent to the carbonyl

group. The same is true of 5-chloro-1:3:6-trimethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one (m. p. 142—143°), which is obtained by chlorination of 1:3:6-trimethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one.

5:6-Dibromo-1-methyl-1-dichloromethyl- Δ^2 -cyclohexen-4-one, which, when freshly prepared, forms colourless needles, m. p. 80—81°, is obtained by allowing equimolecular quantities of 1-methyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one and bromine to combine in carbon disulphide, and, when boiled with potassium acetate and acetic acid, is converted into 5-bromo-1-methyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one, which has m. p. 89—90°, b. p. 183—185°/15 mm. The *p*-nitrophenylhydrazone melts at 154—156°. On treatment with magnesium and methyl iodide, the ketone is converted into 5-bromo-1:4-dimethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol, which forms slender, colourless needles, m. p. 103—104°, and is somewhat less stable than its chlorine analogue.

2:3:5:6-Tetrabromo-1-methyl-1-dichloromethylcyclohexan-4-one is obtained in "*cis*." and "*cis-trans*." modifications by the action of four atoms of bromine on 1-methyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one. The former crystallises in rosettes of colourless needles, m. p. 137° (decomp.), and the latter in needles which immediately after crystallisation melt at 118—119°. This compound does not keep well, however. When either isomeride or the original crude bromine additive product is boiled with potassium acetate and acetic acid, hydrogen bromide is eliminated and 3:5-dibromo-1-methyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one is produced. This substance forms prisms or tablets, m. p. 120—121°, and is stable towards excess of bromine at 100°. It may be prepared in small yield by the action of chloroform and sodium hydride on *oo*-dibromo-*p*-cresol, and when treated with magnesium and methyl iodide is converted into 3:5-dibromo-1:4-dimethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol, which crystallises in needles, m. p. 91—92°, and eliminates water only at 250°.

The product of addition of two atoms of bromine to 1:3-dimethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one is too unstable to admit of its being isolated, and passes under the conditions of its formation into 5-bromo-1:3-dimethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one, which has m. p. 65—66°, b. p. 180—185°/13 mm., and in agreement with the position assigned to the bromine atom, shows no tendency to react with *p*-nitrophenylhydrazine.

C. K. I.

The Mutual Replacement of Amine Residues by Anils.
G. REDDELIEN (*Ber.*, 1921, 54, [B], 3121—3131).—It has been shown previously (A., 1910, i, 118; 1913, i, 1203) that the formation of ketoneanils can be facilitated greatly by the presence of a suitable catalyst, such as aniline zincchloride or halogen acid, but the procedure gives poor yields with many ketones of high molecular weight and substituted anilines by reason of the slowness of the change. The desired anils may, however, be obtained readily if the simple ketoneanils (in place of the ketones themselves) are

heated with the requisite amine. The process appears to take place in accordance with the scheme: $R_2C \cdot NPh + H_2N \cdot R^1 = R_2C(NHR^1) \cdot NPh = R_2C \cdot NR^1 + NH_2Ph$. The conditions which govern the course of the change are the volatility of the amine, the chemical affinity to the ketonic or aldehydic residue, and the concentration of the amine. If the eliminated amine is not removed (for example, by distillation), an equilibrium governed by the law of mass action becomes established. The replacement of a less by a more volatile amine can, however, be secured if the latter is used in large excess. The amine residue of ketoneanils can be removed by amino-acids in a similar manner; the process does not depend on the activity of the carboxyl groups, since the fission of ketoneanils by carboxylic acids occurs with much less readiness. The new process can be utilised for the production of ketoneanils which, by reason of steric hindrance, are not obtainable directly from the ketones, the starting point being the ketoneimine. The displacements can be catalytically accelerated by aniline zinc-chloride or halogen acids, but this is not generally necessary. The reaction may also be extended to acid amides, the same catalysts being operative.

Benzophenone-β-naphthyl, $CPh_2 \cdot N \cdot C_{10}H_7$, short, greenish-yellow prisms, m. p. 96.5° , is prepared by heating a mixture of benzophenoneanil and β-naphthylamine ultimately to 180° in a vacuum. *Fluorenylidene-p-aminodiphenyl*, $C(C_6H_4)_2 \cdot N \cdot C_6H_4Ph$, from fluorenoneanil and *p*-aminodiphenyl, crystallises in short, golden-yellow prisms, m. p. 186° . *Di-α-naphthylketoneanil*, from di-α-naphthylketoneimine, m. p. 87° , and aniline, forms pale yellow prisms, m. p. 155° . *Di-α-naphthylketone-α-naphthyl*, short, yellow prisms, has m. p. 211° . *Benzophenone-p-anilinoanil*, $CPh_2 \cdot N \cdot C_6H_4 \cdot NPh$, from benzophenoneanil and *p*-aminodiphenylamine, forms dark yellow, oblique, four-sided rods, m. p. 111° . *Benzophenoneanil-p'-carboxylic acid*, $CPh_2 \cdot N \cdot C_6H_4 \cdot CO_2H$, short, pale yellow prisms, m. p. 240° , is obtained readily from *p*-aminobenzoic acid and benzophenoneanil or benzophenoneimine; the sodium salt, an intensely yellow, crystalline powder, and the potassium salt are described. *Fluorenoneanil-p'-carboxylic acid*, from fluorenoneanil and *p*-aminobenzoic acid, crystallises in yellow leaflets, m. p. 253° . *Benzophenoneimine* is prepared conveniently by heating benzophenoneanil at 200° in the presence of a little aniline hydrobromide in a current of dry ammonia. *Fluorenoneimine*, pale yellow, slender needles, m. p. 124° , is prepared in a similar manner. *Benzophenone-methylimide*, $CPh_2 \cdot NMe$, a colourless liquid, b. p. $158-159/13\text{ mm.}$, is obtained by heating benzophenoneanil and aniline hydrobromide at $200-210^\circ$ in a current of dry methylamine. *Fluorenonemethylimide* crystallises in pale yellow leaflets, m. p. $110-111^\circ$. *Benzophenonebenzoylhydrazone*, $CPh_2 \cdot N \cdot NHBz$, from benzophenoneanil and benzoylhydrazine at 100° , forms small, colourless rods, m. p. 115.5° ; it can also be prepared in almost quantitative yield by protracted ebullition of a solution of its components in alcohol. *Fluorenonebenzoylhydrazone* forms pale yellow needles, m. p. 171° .

H. W.

Fission of Anils. G. REDDELIEN and HILDEGARD DANILOF (*Ber.*, 1921, **54**, [B], 3132—3142; cf. A., 1910, i, 118; 1913, i, 1203, and preceding abstract).—Anils are hydrolysed by aqueous solutions of mineral acids with a readiness which depends to an unusual extent on the presence of substituents. Steric hindrance is shown when the latter are present in the ortho-position, but hydrolysis is also facilitated greatly by positive and retarded by negative groups in the para-position. The stability of substances such as benzophenoneanil-*p*'-carboxylic acid is probably due to a subsidiary valency linking as indicated by the formula $\text{CPh}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, which also renders possible an explanation of the ready fission of the corresponding esters. The anils are much more stable towards alkali than towards acid. The aldehydeanils, however, are hydrolysed more or less completely by protracted heating with sodium hydroxide, whereas certain ketoanils are completely stable even towards the 30% solution. The similarity of the behaviour of the CNPh group in anils with the keto-group has been emphasised previously by Miller and Plöchl (A., 1896, i, 609) and by Reddelien (*loc. cit.*). This, however, does not extend to the behaviour of the substances towards alkali, since the ketones undergo fission with much greater readiness than do the ketoanils. The remarkable stability of the latter towards alkali has caused the authors to investigate the possibility of esterifying hydroxyanils and anil-carboxylic acids and of acylating hydroxyanils and ketoneimides in alkaline solution. Esterification with methyl sulphate proceeds smoothly. Benzoylation according to the Schotten-Baumann method is more complex, since the hydroxyanils suffer fission when the solution is warmed, whereas in cold solution this action is less marked (but never completely suppressed) and the desired benzoates are produced. Acetylation of hydroxyanils with acetic anhydride and sodium acetate occurs invariably with great smoothness.

Benzoylation of the ketoneimines cannot be effected by the Schotten-Baumann method, since benzamide is always produced owing to fission of the imine. The benzoylated products can, however, be prepared in pyridine solution or by the use of benzoic anhydride dissolved in benzene. In contrast to the ketoneimines, they are very stable substances, which are hydrolysed only by boiling acid or alkali.

The anils are also decomposed by hydrogen sulphide in accordance with the equation $\text{CR}_2\text{NPh} + \text{H}_2\text{S} \rightarrow \text{CR}_2\text{S} + \text{NH}_2\text{Ph}$. Reaction occurs with some difficulty, and not invariably in warm alcoholic solution, and is effected preferably by passing hydrogen sulphide through a suspension of the anil salt in benzene.

The following individual substances are described. Benzophenone-*p*-dimethylaminoanil, $\text{CPh}_2\text{N}(\text{C}_6\text{H}_4\text{NMe}_2)$, yellow crystals, m. p. 86—87°, which is obtained conveniently from benzophenone, dimethyl-*p*-phenylenediamine, and hydrobromic acid at 160—180° (cf. Reddelien, A., 1910, i, 118; Moore, A., 1910, i, 281). *Ethyl benzophenoneanil-p'*-carboxylate, $\text{CPh}_2\text{N}(\text{C}_6\text{H}_4\text{CO}_2\text{Et})$ (from benzophenoneanil and ethyl *p*-aminobenzoate in a vacuum at 180—200°),

small, yellow needles, m. p. 93—94°. *Methyl benzophenoneanil-p'-carboxylate* (from the acid, methyl sulphate, and sodium hydroxide), pale yellow leaflets, m. p. 133°. *Methyl fluorenoneanil-p'-carboxylate*, $C_{12}H_9 \cdot N \cdot C_6H_4 \cdot CO_2Me$, yellow leaflets, m. p. 170°. *Ethyl benzylidene-p-aminobenzoate*, $CHPh \cdot N \cdot C_6H_4 \cdot CO_2Et$, pale yellow needles, m. p. 47°. *Benzylidene-p-anisidine*, m. p. 72°. *Benzo-phenonebenzoylimide*, $CPh_2 \cdot N \cdot Bz$, colourless prisms, m. p. 117—118°. *Fluorenonebenzoylimide*, pale yellow leaflets, m. p. 130°. *Benzylidene-p-aminophenyl benzoate*, $CHPh \cdot N \cdot C_6H_4 \cdot OBz$, colourless needles, m. p. 144°. The *benzoate*, pale yellow leaflets, m. p. 105°, and *acetate*, pale yellow prisms, m. p. 93—94°, of benzophenone-*p*-hydroxyanil. Benzilmonoanil is converted by potassium hydroxide at 170—180° into benzilic and anilindiphenylacetic acids.

Benzophenoneanil hydrochloride is transformed by hydrogen sulphide into thiobenzophenone, a dark blue liquid, b. p. 176—178°/18 mm. In a similar manner, *p*-dimethylaminobenzophenoneanil hydrochloride, red needles, m. p. 178° (decomp.), is converted into *p*-dimethylaminothiobenzophenone, $C_{15}H_{15}NS$, bluish-red, rhombic leaflets, m. p. 91°.

Thiobenzophenone is also produced when hydrogen sulphide is passed through molten benzophenoneanil, but the action proceeds further to the formation of diphenylmethane, $CPh_2 \cdot S + H_2S = CH_2Ph_2 + S_2$. Under similar conditions, fluorenoneanil gives a red sulphide which could not be isolated in a homogeneous condition

and dithiodifluorenone $\begin{array}{c} C_6H_4 \\ \diagup \quad \diagdown \\ C \quad S \\ \diagdown \quad \diagup \\ C_6H_4 \end{array} < \begin{array}{c} S \\ \diagup \quad \diagdown \\ C \quad S \\ \diagdown \quad \diagup \\ C_6H_4 \end{array} < \begin{array}{c} C_6H_4 \\ \diagup \quad \diagdown \\ C \quad S \\ \diagdown \quad \diagup \\ C_6H_4 \end{array}$ (cf. Smedley, T., 1905, 87, 1253).

H. W.

Dibenzylideneacetone [Distyryl Ketone] and Triphenylmethane. X. Ionogenically Linked Halogen Atoms. FRITZ STRAUS and AMADÄUS DÜTZMANN (*J. pr. Chem.*, 1921, [ii], 103, 1—68; cf. A., 1912, i, 989).—The unsaturated chlorides obtained by the action of phosphorus pentachloride on distyryl ketone and other ketones of similar structure contain the group $CHCl$, and are derived from diphenylchloromethane by the separation of one of the benzene nuclei from the methane carbon atom by a more or less long, conjugated chain of ethylene linkings. In the reactions of these unsaturated chloro-compounds, the secondary chlorine atom exhibits a highly developed "ionogenic" linking closely resembling that observed with triphenylchloromethane. Thus, the chlorine atom is readily replaceable by hydroxyl, methoxyl, another halogen, etc., and also induces in the compounds ability to unite with compounds of different character, forming intensely coloured complexes. Among the latter, a special position is occupied by the additive compounds formed with sulphur dioxide, the coloured solutions of these compounds in excess of the liquefied gas exhibiting electrical conductivity; in a few instances, such compounds may be isolated and analysed.

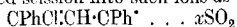
The authors have measured the conductivities of a considerable number of these solutions with the object of determining the manner in which the conductivity varies with constitutive altera-

tion in the molecular structure of the unsaturated chloro-compounds (cf. Straus and Hüsey, A., 1909, i, 490). Benzyl chloride and diphenylchloromethane, which may be regarded as the parent substances of the whole series, show no measurable conductivity even in concentrated solution. Conductivity makes its appearance when an ethylene linking is introduced between the methyl carbon atom and the one nucleus, and increases with the number of such linkings in the molecule until it assumes considerable magnitude. As regards the influence of nuclear substituents on the conductivity of these unsaturated chloro-compounds, the only data available refer to compounds in which either chlorine or methoxyl is introduced in the para-position in both nuclei; such data show that the conductivity is diminished by chlorine, but is increased by methoxyl to the order of magnitude of the conductivities exhibited by the best-conducting true salts. Thus, the influence of nuclear methoxyl suppresses all other constitutive influences.

Of the effects on the conductivity of change of the anion little is known. Replacement of the secondary chlorine by bromine results in considerable augmentation of the conductivity. The carbinols obtained by treating the chloro- or bromo-compounds with water also dissolve in liquid sulphur dioxide, giving coloured complex compounds, the conductivities of which are approximately 10% of those of the corresponding chloro-compounds. The methyl ethers of the carbinols give coloured and conducting solutions in sulphur dioxide only when they correspond with highly conducting chlorides; the molecular conductivities of such ethers are about one-half as great as those of the corresponding carbinols, but persistently increase, instead of remaining constant, for any definite dilution.

The magnitudes of the conductivities of these coloured solutions exhibit parallelism with the intensities of their colour, these varying, for solutions of the different compounds of similar concentrations, to the same degree as the molecular conductivities. Indeed, in all the cases investigated, gradual diminution of the conductivity is accompanied by fading of the colour; further, with the carbinols examined and with triphenylcarbinol, which give solutions at first colourless, the subsequent change into coloured solutions corresponds with measurable increases in the conductivity. It is therefore assumed that, even in solutions of the chlorides in liquid sulphur dioxide, an equilibrium exists between a colourless, non-conducting form, which may be regarded as formed by heterogeneous association between molecules of the chloride and of the solvent, and represents simple solution such as occurs with organic solvents, and a second, coloured, conducting form, arising by transformation of the solvate originally formed, $\text{:CHCl} \dots \text{xSO}_2$ (colourless) \rightleftharpoons $\text{:CHCl} \dots \text{xSO}_2$ (coloured). With the chlorides themselves, the establishment of this equilibrium proceeds too rapidly to permit of direct observation. In considering the observed variation of the conductivity, it must be borne in mind that dilution causes, not only the normal increase in the dissociation, but also a simultaneous displacement of the equilibrium between colourless and coloured forms.

The results of Hantzsch's investigations (A., 1918, ii, 2, 4) show that the process of ionisation does not, of itself, condition alteration of the light absorption, and that with a coloured ion there must correspond a coloured non-dissociated parent form. Hence, in the coloured solutions of these chlorides in sulphur dioxide, the presence of a second, coloured, ionisable compound must be assumed. As yet it has not been found possible to prove experimentally the assumed scission into such ions as



and $\text{Cl}^- \dots x\text{SO}_2$, by electrolysis of one of these chlorides (cf. Schlenk, A., 1910, i, 236).

The investigation of the velocities with which these halogen compounds are decomposed by water (A., 1909, i, 490; 1910, i, 593; 1912, i, 989) yielded results which, together with those now obtained, indicate that similar alterations in the molecules of the halogen compounds or, in other words, similar alterations in the affinity demands of the methyl carbon atom, influence the velocity of the decomposition by water and the electrical conductivity qualitatively in the same direction.

The conclusions drawn by Straus, Lutz, and Hüsey (A., 1910, i, 563) regarding the dependence of the stability of the coloured complex compounds formed by various chlorides on the number of unsaturated linkings and on the nature of the substitution in the nucleus are confirmed.

According to Werner's hypothesis, the hydrolysis of the complex chlorides results first in a loose union of the water molecule with the chlorine atom, this proceeding to varying extents with the different chlorides; the affinities are then brought into equilibrium by the formation of the carbinol rather than by displacement of an electron: $\text{R}_1\text{R}_2\text{H:C:Cl} \dots \text{HOH} \longrightarrow \text{R}_1\text{R}_2\text{H:C} \overset{\curvearrowright}{\text{Cl}} \cdot \text{H OH}$.

The phenomena observed with the unsaturated chlorides in solution in sulphur dioxide are discussed in relation to the halochromy of the unsaturated ketones, and it is found that the conductivities of sulphur dioxide solutions of these chlorides are extremely small and bear no relationship to those of the corresponding chlorides.

Walden (A., 1902, i, 536) drew the conclusion that the capacity of these chlorides to undergo electrolytic dissociation is determined principally by the number of radicles united to the carbon atom, and that only tertiary compounds exhibit appreciable electrical conductivity. The authors' results show, however, that secondary halogen compounds also may display the properties of strong electrolytes.

A full description is given of the methods employed in the conductivity measurements which have been applied to: (I) Derivatives of diphenylmethane and fluorenone: diphenylchloromethane; the chloride of 4:4'-diphenylbenzophenone, $\text{CCl}_2(\text{C}_6\text{H}_4\text{Ph})_2$; *p*:*p*'-dimethoxybenzophenone and the corresponding dichloro-compound, $\text{CCl}_2(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, and monochloro-compound, $\text{CHCl}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$; the chloride of fluorenone. (II) Derivatives of phenyl styryl

ketone: $\alpha\gamma$ -dichloro- $\alpha\gamma$ -diphenylpropylene; $\alpha\gamma$ -dichloro- $\alpha\gamma$ -di-*p*-chlorophenylpropylene; α -chloro- γ -bromo- $\alpha\gamma$ -di-*p*-chlorophenylpropylene; *p*-anisyl *p*-methoxystyryl ketone; $\alpha\gamma$ -dichloro- $\alpha\gamma$ -di-*p*-anisylpropylene; α -chloro- γ -bromo- $\alpha\gamma$ -di-*p*-anisylpropylene; $\alpha\gamma$ -dibromo- $\alpha\gamma$ -di-*p*-anisylpropylene. (III) Derivatives of distyryl ketone and of phenyl cinnamylidenemethyl ketone: $\gamma\epsilon$ -dichloro- $\alpha\epsilon$ -diphenyl- $\Delta^{\alpha\gamma}$ -pentadiene; γ -chloro- $\alpha\epsilon$ -diphenyl- $\Delta^{\alpha\gamma}$ -pentadiene- ϵ -ol, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}\cdot\text{CCl}\cdot\text{CH}\cdot\text{CHPh}$, and its methyl ether; $\gamma\epsilon$ -dichloro- $\alpha\epsilon$ -di-*p*-chlorophenyl- $\Delta^{\alpha\gamma}$ -pentadiene; γ -chloro- $\alpha\epsilon$ -di-*p*-chlorophenyl- $\Delta^{\alpha\gamma}$ -pentadiene- ϵ -ol, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{CCl}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Cl}$, and its methyl ether; ϵ -chloro- $\alpha\epsilon$ -di-*p*-chlorophenyl- $\Delta^{\alpha\gamma}$ -pentadiene; dianisylidenemethyl ketone; $\gamma\epsilon$ -dichloro- $\alpha\epsilon$ -di-*p*-anisyl- $\Delta^{\alpha\gamma}$ -pentadiene; γ -chloro- ϵ -methoxy- $\alpha\epsilon$ -di-*p*-anisyl- $\Delta^{\alpha\gamma}$ -pentadiene. (IV) Derivatives of dicinnamylidenemethyl ketone: $\alpha\epsilon$ -dichloro- $\alpha\epsilon$ -diphenyl- $\Delta^{\alpha\gamma\eta}$ -nonatetrene; ϵ -chloro- $\alpha\epsilon$ -diphenyl- $\Delta^{\alpha\gamma\eta}$ -nonatetrene- ϵ -ol, and its methyl ether. (V) Tridiphenylchloromethane.

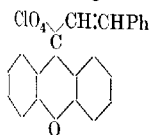
T. H. P.

Halochromic Phenomena with Diarylstyrylcarbinols.

KARL ZIEGLER (*Ber.*, 1921, **54**, [B], 3003—3009).—The recent publication of Hess and Weltzien (this vol., i, 35) has induced the author to put forward an account of his work in this field. It is based on the hypothesis that the halochromy of the triarylcarbinols is connected with the possibility of existence of the triarylmethyls, and that the cause is to be found in the unsaturated nature of the benzene nucleus. If this is the case, it should be possible to replace the latter by unsaturated groups without disturbance of the typical properties of the substances. This has been achieved in a number of instances by the aid of the styryl complex.

Benzophenone gives with the magnesium compound of β -bromostyrene a compound which becomes intensely red and then green when treated with concentrated sulphuric acid, the colour disappearing on addition of water. A similar substance is derived from phenyl *p*-tolyl ketone, but not from acetophenone, thus conforming to theory. The compounds have not been isolated in the homogeneous condition.

[With KURT OCHS.]—The Grignard reagent from β -bromostyrene gives with 4:4'-dimethoxybenzophenone in ethereal solution *di-p*-anisylstyrylcarbinol, $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2\cdot\text{CH}\cdot\text{CHPh}$, which is isolated in the form of its perchlorate, a stable, dark red powder, m. p. about 90° . The salt gives a magenta-red solution in acetone or chloroform, which is stable in the cold but rapidly becomes discoloured when warmed. The similar compounds from other diaryl ketones all give magenta-red solutions, but the isolation of other crystalline perchlorates has not been effected. 9-Styrylxanthene perchlorate (annexed formula) is obtained similarly from xanthone: it forms red prisms or thin, orange-yellow leaflets, decomp. 187 — 189° . The substance is remarkably stable. When boiled with alcohol, it is converted into *ms*-styrylxanthene, m. p. 215° . 9-Styryl-1-meth-



oxyzanthenyl perchlorate is a stable, dark red powder which softens at 160° and becomes black, without melting, at 250°. *9-Styryldi-ββ'-naphthoxanthenyl perchlorate* is somewhat less stable. H. W.

The Beckmann Transformation. JAKOB MEISENHEIMER (*Ber.*, 1921, 54, [B], 3206—3213).—Two stereoisomeric forms of benzilmonoxime are known and, in accordance with the results of the Beckmann transformation, the formulæ $\text{Ph}\cdot\overset{\text{O}}{\underset{\text{HO}\cdot\text{N}}{\text{C}}}\cdot\text{Bz}$ and $\text{Ph}\cdot\overset{\text{O}}{\underset{\text{N}\cdot\text{OH}}{\text{C}}}\cdot\text{Bz}$

have been assigned to the β- and α-forms. It has been assumed that intramolecular reactions take place with greater readiness when the reacting groups are disposed near to one another in space, but this has never been proved strictly to be the case. The incidental observation that 3:4:5-triphenylisooxazole is converted by chromic acid in glacial acetic acid solution or by ozone into benzoyl-β-benzilmonoxime, $\text{Ph}\cdot\overset{\text{O}}{\underset{\text{N}\cdot\text{O}\cdot\text{C}\cdot\text{Ph}}{\text{C}}}\cdot\text{Ph} \rightarrow \text{Ph}\cdot\overset{\text{O}}{\underset{\text{N}\cdot\text{OBz}}{\text{C}}}\cdot\text{CO}\cdot\text{Ph}$

(Meisenheimer, this vol., i, 176), proves, however, that the configurations assigned previously to the benzilmonoximes are incorrect, and that, during the Beckmann change, the transformation occurs, not between vicinal groups, but between those placed in the *anti*-position to one another. It is hereby assumed that in the opening of a ring only one form can be produced, which must contain the developed groups in the vicinal position to one another; the necessary precautions have been taken to prove that the benzoyl-benzilmonoxime is actually the primary product of the fission of 3:4:5-triphenylisooxazole.

The new view of the course of the Beckmann change necessitates a redistribution of the formulæ among the benzildioximes, the α-, β-, and γ-forms now receiving the configurations $\text{Ph}\cdot\overset{\text{O}}{\underset{\text{HO}\cdot\text{N}}{\text{C}}}\cdot\overset{\text{O}}{\underset{\text{N}\cdot\text{OH}}{\text{C}}}\cdot\text{Ph}$

$\text{Ph}\cdot\overset{\text{O}}{\underset{\text{N}\cdot\text{OH}}{\text{C}}}\cdot\text{C}\cdot\text{Ph}$, $\text{Ph}\cdot\overset{\text{O}}{\underset{\text{HO}\cdot\text{N}}{\text{C}}}\cdot\overset{\text{O}}{\underset{\text{N}\cdot\text{OH}}{\text{C}}}\cdot\text{Ph}$, respectively, thus involving the transpositions of the formulæ assigned previously to the α- and β-forms, whilst leaving that of the γ-variety unchanged. A review of the literature on the subject shows that the chemical behaviour of the dioximes is in much better accord with the new than with the older formulæ.

The mechanism of the Beckmann transformation is now explained in the following manner. In the oximes, the radicals attached to the vicinal carbon atom, for example, the phenyl group of α-benzilmonoxime, exert an attraction on the hydroxyl group, and thus displace it from its normal position. The residual or partial valency of the nitrogen atom on the side remote from the hydroxy-group is thereby strengthened. In certain circumstances (the best conditions for the Beckmann change), the residual valency becomes so powerful that it attracts the vicinal group attached to the carbon atom to itself. Momentarily, therefore, a compound, $\text{Ph}\cdot\overset{\text{O}}{\underset{\text{X}\cdot\text{N}\cdot\text{Bz}}{\text{C}}}\cdot\text{C}\cdot\text{Ph}$, with tervalent carbon and quadrivalent nitrogen is pro-

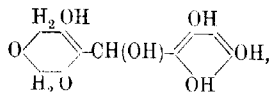
duced. In the latter, the radicle X attached to the nitrogen by oxygen has but little relationship to the nitrogen, and is therefore eliminated and naturally becomes attached to the tervalent carbon atom.

Triphenylisooxazole, dissolved in carbon tetrachloride, is converted by successive treatment with ozone and water into benzoyl- β -benzilmonoxime, m. p. $137.5-138.5^\circ$, in addition to a little oxalic and benzoic acids. The oxime and benzoic acids are also produced when the isooxazole is oxidised with chromic acid in glacial acetic acid solution, but the yields are very small. Benzoyl- β -benzilmonoxime is obtained conveniently by the action of benzoyl chloride on the oxime in the presence of pyridine. Under similar conditions, α -benzilmonoxime gives a compound of the expected composition, which, however, is probably ON-dibenzoylisobenzamide, OBz·CPh:Nbz, m. p. $95-96^\circ$ (cf. Werner and Piguet, A., 1905, i, 66). Benzoyl- β -benzilmonoxime is converted by sodium hydroxide in aqueous alcoholic solution almost quantitatively into the β -oxime and benzoic acid. Under similar conditions, the benzoyl compound obtained from the α -oxime gives benzonitrile and benzoic acid.

H. W.

Condensation Reactions of Formic Acid. ERW. SCHWENK (*J. pr. Chem.*, 1921, [ii], **103**, 103-105).—That the condensation reaction of formic acid with 2-methylindole (Scholtz, A., 1913, i, 893) is not confined to such pyrrole derivatives is shown by the behaviour of formic acid in presence of concentrated sulphuric acid towards 3-oxythionaphthen and towards phloroglucinol. In the first case, the product of the reaction is the 3-oxythionaphthen-1-aldehydethioindogenide, m. p. about 270° , obtained by Friedländer and Kielbasinski (A., 1911, i, 1021) from 3-oxythionaphthen-1-aldehyde and acids, and by Friedländer and Risse (A., 1914, i, 876) by the action of chloroform and an alkali on 3-oxythionaphthen; this compound forms an *acetyl* derivative, $C_{17}H_{10}O_2S_2$, m. p. 211° .

The action of formic acid on phloroglucinol in presence of sulphuric acid yields an orange, pulverulent compound, $C_{13}H_{12}O_7$, possibly



which does not melt at 300° , and at 150° is converted into the compound, $C_{13}H_{10}O_6$.

T. H. P.

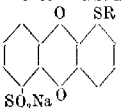
Preparation of Hydroxyanthraquinones from Nitroanthraquinones. ERW. SCHWENK (*J. pr. Chem.*, 1921, [ii], **103**, 106-108).—The methods which have been suggested for replacing the nitro-groups of nitroanthraquinones by hydroxyl groups give either poor yields or impure products, or are tedious to execute. The author finds, however, that this replacement may be readily effected by prolonged heating of the nitro-compound with potassium

acetate and acetic acid in an oil-bath at 170–180°. The nitro-group is doubtless replaced first by acetyl, but in no instance could the acetyl compound be isolated; the readiness with which the acetyl group is replaced is doubtless related to the difficulty experienced in acetylating the α -hydroxyanthraquinones (Dimroth, Friedmann, and Kämmerer, A., 1920, i, 443). Replacement of nitro-groups by hydroxyls by the action of potassium acetate does not take place in the naphthalene or benzene series; with 3-nitrophthalic acid, a reaction occurs, but this has not been investigated.

T. H. P.

Derivatives of Anthraquinone. Aliphatic Thioethers, Dithioethers, and Thioether Sulphonic Acids. E. EMMET REID, COLIN M. MACKALL, and GEORGE E. MILLER (*J. Amer. Chem. Soc.*, 1921, 43, 2104–2117).—Anthraquinone- α -sulphonic acid and the 1:5- and 1:8-disulphonic acids when heated with aliphatic mercaptans in alkaline solution reacted readily to form thioethers, thioether sulphonic acids, and dithioethers. The reaction takes place rapidly at 100°. The corresponding sulphones were prepared from the thioethers and dithioethers by oxidation with nitric acid. The following compounds are described:

Thioethers, $C_{14}H_7O_2SR$: Anthraquinone methyl thioether, m. p. 221°; anthraquinone ethyl thioether, m. p. 184°; anthraquinone propyl thioether, m. p. 151°; anthraquinone butyl thioether, m. p. 112.5°; anthraquinone isobutyl thioether, m. p. 144°; anthraquinone isoamyl thioether, m. p. 86°. The corresponding sulphones, $C_{14}H_7O_2SO_2R$, are: methyl, m. p. 254°; ethyl, m. p. 211.5°; propyl, m. p. 204.5°; butyl, 150°; isobutyl, m. p. 190°; isoamyl, m. p. 133°.

The anthraquinone-5-sulphonic acid 1-alkyl thioethers, , were isolated in the form of various salts as follows:

Anthraquinone-5-sulphonic acid 1-methyl thioether as its sodium, barium, aniline, m. p. 290–299° (decomp.), o-toluidine, m. p. 285–290° (decomp.), and p-toluidine, m. p. 298–304° (decomp.), salts. *Anthraquinone-5-sulphonic acid 1-ethyl thioether* as its sodium, barium, aniline, m. p. 276–285° (decomp.), o-toluidine, m. p. 264–274° (decomp.), and p-toluidine, m. p. 276–285° (decomp.), salts. *Anthraquinone-5-sulphonic acid 1-propyl thioether* as its sodium, barium, aniline, m. p. 270–277° (decomp.), o-toluidine, m. p. 255–257° (decomp.), and p-toluidine salts. *Anthraquinone-5-sulphonic acid 1-butyl thioether* as its sodium, barium, strontium, calcium, aniline, m. p. 257–259° (decomp.), o-toluidine, m. p. 234–237° (decomp.), and p-toluidine, m. p. 256–260° (decomp.), salts. *Anthraquinone-5-sulphonic acid 1-isoamyl thioether* as its sodium, barium, aniline, m. p. 263–265° (decomp.), o-toluidine, m. p. 250–254° (decomp.), and p-toluidine, m. p. 267–277° (decomp.), salts.

1:5-Anthraquinone dialkyl dithioethers: dimethyl; methyl ethyl,

m. p. 229°; *methyl propyl*, m. p. 209°; *methyl butyl*, m. p. 173.5°; *methyl isoamyl*, m. p. 175°; *diethyl*, m. p. 226.5°; *ethyl propyl*, m. p. 188.5°; *ethyl butyl*, m. p. 156°; *ethyl isoamyl*, m. p. 152°; *dipropyl*, m. p. 227°; *propyl butyl*, m. p. 175°; *dibutyl*, m. p. 159.5°; *butyl isoamyl*, m. p. 134°, and *di-isoamyl*, m. p. 158.5°. The corresponding disulphones are *dimethyl*; *methyl ethyl*, m. p. > 300°; *methyl propyl*, m. p. 291°; *methyl butyl*, m. p. 264°; *methyl isoamyl*, m. p. 266°; *diethyl*, m. p. 269.5°; *ethyl propyl*, m. p. 243.5°; *ethyl butyl*, m. p. 194°; *ethyl isoamyl*, m. p. 198°; *dipropyl*, m. p. 265°; *propyl butyl*, m. p. 220°; *dibutyl*, m. p. 184.5°; *butyl isoamyl*, m. p. 203.5°, and *diisoamyl*, m. p. 202°.

The anthraquinone-8-sulphonic acid 1-alkyl thioethers prepared are as follows: 1-*methyl* as its *sodium*, *barium*, *aniline*, m. p. 260° (decomp.), *o-toluidine*, m. p. 255° (decomp.), and *p-toluidine*, m. p. 260° (decomp.), salts; 1-*ethyl* as its *sodium*, *barium*, *aniline*, m. p. 250° (decomp.), *o-toluidine*, m. p. 260° (decomp.), and *p-toluidine*, m. p. 255°, salts; 1-*propyl* as its *sodium*, *barium*, *aniline*, m. p. 242° (decomp.), *o-toluidine*, m. p. 260° (decomp.), and *p-toluidine*, m. p. 260° (decomp.), salts; 1-*butyl* as its *sodium*, *barium*, *strontium*, *calcium*, *lead*, *nickel*, *cobalt*, *copper*, *aniline*, m. p. 260° (decomp.), *o-toluidine*, m. p. 260° (decomp.), and *p-toluidine*, m. p. 255° (decomp.), salts; and 1-*isoamyl* as its *sodium* and *barium* salts.

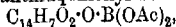
The 1:8-anthraquinone dialkyl dithioethers are: *dimethyl*, m. p. 222°; *methyl ethyl*, m. p. 210°; *methyl propyl*, m. p. 173.5°; *methyl butyl*, m. p. 134°; *methyl isoamyl*, m. p. 114°; *diethyl*, m. p. 167.5°; *ethyl butyl*, m. p. 95°; *dipropyl*, m. p. 142°; *propyl butyl*, m. p. 119.5°; *propyl isoamyl*, m. p. 104°; *dibutyl*, m. p. 131°; *butyl isobutyl*, m. p. 103.5°; *butyl isoamyl*, m. p. 116.5°, and *di-isoamyl*, m. p. 133°. The corresponding disulphones are: *dimethyl*, m. p. 310°; *methyl ethyl*, m. p. 220°; *methyl propyl*, m. p. 211°; *methyl butyl*, m. p. 169°; *methyl isoamyl*, m. p. 172°; *diethyl*, m. p. 228°; *ethyl butyl*, 128°; *dipropyl*, m. p. 210°; *propyl butyl*, m. p. 200.5°; *propyl isoamyl*, m. p. 147.5°; *dibutyl*, m. p. 138°; *butyl isobutyl*, m. p. 168.5°; *butyl isoamyl*, m. p. 154° and *diisoamyl*, m. p. 176°.

Attempts were made to prepare similar derivatives from sodium naphthalene- α -sulphonate, but no reaction took place. Preliminary experiments showed that when sodium anthraquinone- α -sulphonate was replaced by the β -sulphonate replacement by the mercaptan residue took place with much greater difficulty, if at all.

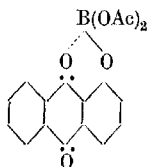
W. G.

Boric Esters of Hydroxyanthraquinones. OTTO DIMROTH and THEO FAUST (*Ber.*, 1921, **54**, [B], 3020-3034).—Boric acid is used extensively in the chemistry of the hydroxyanthraquinones as a protective agent in oxidations and as accelerator in condensations and nitrations. Its action has been attributed frequently to the formation of boric esters, but the question does not appear to have been investigated systematically. It is now shown that boric esters of the hydroxyanthraquinones can be obtained conveniently from the latter by the action of a solution of boric acid

in acetic anhydride. Thus, 1-hydroxyanthraquinone is transformed into 1-hydroxyanthraquinonyl boroacetate,



which loses a molecule of acetic anhydride when heated in a vacuum, and forms 1-hydroxyanthraquinonyl metaborate, $C_{14}H_7O_2 \cdot O \cdot B(O)O$. 2-Hydroxyanthraquinone, on the other hand, does not react with boric acid. This difference between the behaviour of hydroxy-groups in positions 1 and 2 is characteristic and general. The unusual greater reactivity of the 1-hydroxy-group is explained by the hypothesis that a subsidiary valency union occurs between the boron atom and the ketonic oxygen atom, thus giving rise to compounds of the type indicated by the annexed formula, which are thus analogous to the compounds with tin tetrachloride described by Pfeiffer (A., 1913, i, 879). The correctness of this supposition is supported by the observations that anthraquinone itself reacts with boroacetic anhydride (the compound formed could not be isolated), that 1:5-dihydroxyanthraquinone reacts with two molecules of boroacetic anhydride, whereas



the 1:8-compound reacts with only one molecule, and that 1:4:5-trihydroxyanthraquinone unites with two molecules of boric acid, whilst the third hydroxy-group becomes acetylated.

The formation of boric esters of hydroxyanthraquinones in acetic acid solution is accompanied by characteristic changes in colour and spectrum. Investigation of the latter is not yet complete, but it is established that all diborates are distinguished by very sharp and characteristic absorption bands.

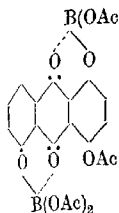
It is remarkable that an α -hydroxy-group in 1:8-dihydroxyanthraquinone is acetylated readily by warming for a short time with boric acid-acetic anhydride solution, whereas such groups are generally difficult to acetylate. In acetic anhydride solution, it is found that 1:8-dihydroxyanthraquinone is more readily mono-acetylated than the 1:5-compound. In general, the author is inclined to attribute the difficulty of acetylating and alkylating α -hydroxyketones to chemical rather than to steric effects, and suggests the possibility of an unstable, subsidiary valency bond between the hydrogen of the hydroxyl group and the ketonic oxygen atom.

The analysis of the hydroxyanthraquinonyl boroacetates is effected by decomposing them with water and weighing the precipitated hydroxyanthraquinone. Acetic acid is estimated in the filtrate by titration with alkali until neutral red becomes yellow, after which mannitol and phenolphthalein are added and the titration is continued until the solution becomes pink.

1-Hydroxyanthraquinonyl boroacetate, orange-red plates, which decomposes when heated without showing a definite melting point, is prepared by gently warming 1-hydroxyanthraquinone with a solution of boroacetic anhydride in an excess of acetic anhydride; it is very readily hydrolysed by water and is unstable towards moist air. It loses acetic anhydride when preserved in a desiccator, rapidly when heated in a vacuum, and passes into 1-hydroxyanthra-

quinonyl metaborate, brown crystals which are much more stable towards water than is the boroacetate. 1:4-Dihydroxyanthraquinonyl diboroacetate forms coarse, ruby-red crystals, whilst the corresponding di-metaborate is rust-brown. Alizarin 1-boroacetate forms dark red crystals which are extremely sensitive to moisture. 2-Acetylalizarin-1-boroacetate, orange-red crystals, is decomposed by water into 2-acetylalizarin, m. p. 198°, acetic acid, and boric acid. Purpuren-1:4-diboroacetate, purple-red crystals, and 2-acetyl-purpuren 1:4-diboroacetate, dark red to violet-red crystals, are also described. Anthrarufindiboroacetate crystallises in golden-yellow,

iridescent leaflets. Chrysazin-monoboroacetate, pale red crystals with a dull golden glance, and 8-acetylchrysazin-1-boroacetate, red crystals, are described; the latter, when hydrolysed, gives 1-hydroxy-8-acetoxyanthraquinone, orange-yellow prisms, m. p. 178°, or lemon-yellow needles, m. p. 179° (the two modifications are interconvertible). 4-Acetoxy-1:5-dihydroxyanthraquinonyl diboroacetate (annexed formula), rust-brown crystals with golden glance, is hydrolysed by water to 1:5-dihydroxy-4-acetoxyanthraquinone, yellow needles, m. p. 165°; the position of the hydroxy-groups in the latter follows from its inability to be oxidised by lead tetra-acetate to a quinone.



H. W.

Researches on Residual Affinity and Co-ordination. VII. Lobaric Lakes of the Alizarin Series. GILBERT T. MORGAN and J. D. MAIN SMITH (T., 1922, 121, 160—169).

The Action of Bromine on Quinizarin and Alizarin. OTTO DIBROTH, ERNST SCHULTZE, and FRITZ HEINZE (Ber., 1921, 54, 3035—3050; cf. A., 1916, i, 563; 1920, i, 443).—Quinizarin is unaffected by bromine water at the ordinary temperature, but it is rapidly oxidised by a concentrated solution of bromine in potassium bromide to quinizarinquinone, which is a much more powerful oxidising agent than benzoquinone. Bromine water in presence of free bromine, however, converts quinizarin into quinizarinquinone dibromide, slender, pink needles, m. p. 210—215° (decomp.); this is also formed by boiling quinizarinquinone with an excess of bromine and glacial acetic acid. It is reduced by sulphurous acid to monobromoquinizarin, red needles, m. p. 228—230° (Liebermann and Rüber, A., 1900, i, 451), which forms a diacetyl derivative, pale yellow needles, m. p. 216—218°, whereas treatment with acetic anhydride-sulphuric acid yields dibromodiacetylquinizarin, pale yellow needles, m. p. 270—271°, which is hydrolysed by sulphuric acid to dibromoquinizarin, m. p. 252—253° (Liebermann and Rüber, loc. cit.).

Quinizarin in methyl alcoholic suspension readily reacts with bromine with ice cooling, forming quinizarinquinone methoxybromide, yellow crystals, m. p. 96°, which is converted by acetic anhydride in the cold into 3-bromodiacetylpurpurin 2-methyl ether,

pale yellow crystals, m. p. 145°, hydrolysed by sulphuric acid to 3-bromopurpurin-2-methyl ether, red needles, m. p. 260°.

Alizarin reacts with bromine more readily than does quinizarin and forms 3-bromoalizarin, yellow plates, m. p. 260—261°, when boiled with an acetic acid solution of bromine, but treatment with bromine water, or a potassium bromide solution of bromine, or bromine water and free bromine yields in each case 3-bromoalizarin-quinone, very sparingly soluble, yellow needles which readily decompose. Alizarinquinone methoxybromide, obtained in a similar manner to the corresponding quinizarin derivative, forms lanceolate, yellow needles, m. p. 230°, after decomposing and sintering at 200°. A methyl-alcoholic suspension of alizarin, on the other hand, when treated with bromine without cooling, yields 3:4-dibromoalizarin, yellow needles, m. p. 251—252°; diacetyl derivative, pale yellow rosettes of needles, m. p. 199—200°; 3:4-dibromoalizarinquinone, yellow crystals.

Alizarin in ethyl alcoholic suspension reacts with bromine with cooling, with formation of alizarinquinone ethoxybromide, yellow tables, m. p. 205° with decomp. after sintering at 180°.

F. M. R.

Anthradiquinones and Anthratriquinones. OTTO DIMROTH and VALENTIN HILCKEN (*Ber.*, 1921, 54, 3050—3063; cf. A., 1916, i, 563; 1920, i, 443).—Quinizarinquinone in glacial acetic acid suspension reacts with hydrogen fluoride with formation of 2-fluoroquinizarin, red prisms; diacetyl derivative, slender, yellow needles, m. p. 189°. With benzenesulphonic acid, quinizarinquinone yields quinizarin-2-phenylsulphone, slender, red needles, m. p. 250°; diacetyl derivative, yellow crystals, m. p. 210°. When quinizarinquinone is suspended in acetaldehyde and exposed to sunlight in a closed vessel, monoacetylquinizarin, yellowish-orange needles, m. p. 186°, is formed.

In order to determine the effect of hydroxyl groups on the properties, mono- and di-hydroxyanthradiquinones have been prepared by the oxidation of tri- and tetra-hydroxyanthraquinones respectively with lead tetra-acetate. 6-Hydroxyquinizarinquinone forms small, brownish-yellow crystals, m. p. 215—220° after decomposing and sintering at 200°, and when treated with acetic anhydride-sulphuric acid yields a mixture of hydroxyanthrapurpurin and hydroxyflavopurpurin. 5-Hydroxyquinizarinquinone forms brown needles, m. p. 220° after darkening at 210°. 5:8-Dihydroxyquinizarinquinone could not be isolated from its deep bluish-violet solution in nitrobenzene.

The acetyl derivative of 1:4:5:6:8-pentahydroxyanthraquinone is obtained by oxidising a glacial acetic acid solution of alizarin-bordeaux with lead tetra-acetate and adding an excess of acetic anhydride and sulphuric acid, and, similarly, the diquinones derived from β -monoacetyl-alizarin-bordeaux and anthrapurpurin were only obtained in acetic acid solution.

When 1:2:4:5:8-pentahydroxyanthraquinone and 1:2:4:5:6:8-hexahydroxyanthraquinone are oxidised by air in alkaline solution,

the *tri*- and *tetra*-hydroxyanthraquinones respectively are obtained, and crystallise from aqueous pyridine in dark violet needles. The hydroxy-derivatives of quinizarinquinone are weaker oxidising agents than the parent substance, and the oxidising power varies with the position of the hydroxyl group in the molecule, for 5-hydroxyquinizarinquinone is a weaker oxidising agent than its 6-hydroxy-isomeride. With regard to the rate of oxidation of a hydroxyanthraquinone to a diquinone, the oxidation to an *o*-quinone proceeds more rapidly than the oxidation to a *p*-quinone. When an acetic acid or nitrobenzene solution of a polyhydroxy-anthraquinone, which contains hydroxyl groups in an *ortho*- or *para*-position in both benzene rings, is oxidised with lead tetra-acetate, the blue to bluish-violet diquinone is first formed, but on further oxidation yellow or yellowish-brown solutions of the triquinone are obtained. Solutions of the triquinones derived from 1:4:5:8-tetrahydroxy-, 1:2:5:8-tetrahydroxy-, pentahydroxy-, and hexahydroxy-anthraquinones were obtained in this manner, but the triquinones were not isolated.

F. M. R.

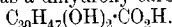
Influence of Substitution in the Components on Equilibria in Binary Solutions. XXXII. The Binary Systems of Camphor with Phenols. ROBERT KREMANN and FRIEDRICH ODELGA (*Monatsh.*, 1921, 42, 147–165; cf. this vol., i, 131).—The fusion diagrams of the binary systems formed by camphor with *p*- and *m*-nitrophenols are completely analogous to that of the system camphor-phenol (Kremann, Wischo, and Paul, A., 1916, i, 217), the curves for the two components falling so steeply that meeting in a simple eutectic is not to be expected; in the region corresponding with 59–69% (for *p*-nitrophenol) or 60–69% (for *m*-nitrophenol) of camphor, no crystallisation is induced by inoculation either with one of the components or with the resorcinol-camphor compound. In almost all cases in which *m*- and *p*-nitrophenols form compounds with a second component, *o*-nitrophenol fails to do so owing to steric hindrance. Hence, if the inability of the camphor-*m*-(or *p*-)nitrophenol system to exhibit crystallisation over the ranges mentioned is due to the existence of a compound seeding with which is impossible, the system camphor-*o*-nitrophenol should form no compound and its fusion diagram should be realisable completely: this is actually the case, the eutectic corresponding with 15° and 54% of camphor. The binary systems formed by camphor with 2:4-dinitrophenol and picric acid show similar behaviour, the eutectics corresponding respectively with 67° and 61% of camphor, and 71° and 60% of camphor; the 2:4-dinitrophenol and picric acid branches exhibit points of inflexion. Here, then, unlike what is observed in other analogous cases, introduction of electronegative nitro-groups into a compound removes the tendency to combine with camphor.

For the systems formed by camphor with pyrogallol and stechol, the fusion curves for the two components descend rapidly and do not meet in a eutectic point on extrapolation. If, however, the intermediate critical viscous melt is seeded with the camphor-

resorcinol compound, a new branch of the diagram of state is realised, this corresponding with the primary crystallisation of a compound of the two components. Contrary to the statements of Efremov (A., 1913, i, 635), the compounds formed are composed of 1 mol. of catechol + 2 mols. of camphor and, apparently, 1 mol. of pyrogallol + 3 mols. of camphor. That the number of molecules of camphor combined should agree with the number of hydroxyl groups in the molecule of the other component is conceivable, but with other compounds, such as amines, steric hindrance to the valency relations results from the ortho-positions of the hydroxyl groups of catechol and pyrogallol, so that the number of molecules of the second component combined is usually less than the number of hydroxyl groups in the hydroxybenzene; in such cases, the two hydroxyl groups act only when they occur in the meta- or para-position. In their behaviour towards camphor, however, the valency activities of the hydroxyls of the dihydroxybenzenes appear to support one another when near and to weaken one another when distant. The fusion curve for the system camphor-quinol exhibits no indication of the formation of the equimolecular compound mentioned by Efremov (*loc. cit.*).

T. H. P.

Saponins. V. Hederin and its Hederagenin. A. W. VAN DER HAAR (*Ber.*, 1921, 54, [B], 3142—3148; cf. A., 1916, i, 41).—It has been shown previously that the crystalline α -hederin is hydrolysed to α -hederagenin, L-arabinose, and rhamnose according to the scheme, $C_{42}H_{66}O_{11} + 3H_2O = C_{31}H_{50}O_4 + C_5H_{10}O_5 + C_6H_{12}O_5$. The previous conclusion that it contains five hydroxyl-groups is somewhat modified, since four of these are found to be capable of acetylation, whereas the fifth is present in the carboxyl group. Since α -hederagenin does not dissolve in aqueous carbonate or bicarbonate solutions, whilst it can be titrated with alkali hydroxide in alcoholic solution, it was considered to be a lactone; this view is now abandoned, since the methyl and ethyl esters are found to contain the two hydroxyl groups present in the original substance, which is now regarded as a dihydroxy-carboxylic acid,

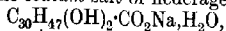


α -Hederin is converted by diazomethane into the corresponding methyl ester, colourless crystals, m. p. 198—200°, which is transformed by acetic anhydride and anhydrous sodium acetate into the tetra-acetyl ester. The sodium salt of α -hederin, $C_{42}H_{65}O_{11}Na \cdot 5H_2O$, and the potassium salt are described.

H. W.

Saponins. VI. Hederagenin. A. W. VAN DER HAAR and A. TAMBURELLO (*Ber.*, 1921, 54, [B], 3148—3158; cf. van der Haar, A., 1916, i, 41, and preceding abstract; Palazzo and Tamburello, *Arch. Farm. Sci. affi.*, 1913, 5, 15).—New analyses of hederagenin have confirmed the formula, $C_{31}H_{50}O_4$, proposed by van der Haar. Diacetylhederagenin loses one of its acetyl groups when heated at 100° or when crystallised from aqueous alcohol, and passes into monoacetylhederagenin, m. p. 156°. The labile

acetyl group appears to be vicinal to the carboxyl-group and to be influenced by its proximity, since the di-acetates of the corresponding methyl and ethyl esters are completely stable towards aqueous alcohol. The sodium salt of hederagenin,



is described. *Hederagenin methyl ester*, $\text{C}_{32}\text{H}_{52}\text{O}_4$ (from the sodium salt and methyl iodide, by the successive action of thionyl chloride and boiling methyl alcohol on the sodium salt, by means of methyl sulphate or by diazomethane), has m. p. 240° , $[\alpha]_D^{25} + 70.9^\circ$ in chloroform solution. *Diacetylhederagenin methyl ester*, $\text{C}_{38}\text{H}_{58}\text{O}_6\cdot\text{H}_2\text{O}$, has m. p. 193° , $[\alpha]_D^{25} + 61.8^\circ$, when dissolved in absolute alcohol. *Hederagenin ethyl ester* crystallises in small, colourless needles, m. p. $218-219^\circ$, $[\alpha]_D^{25} + 72.5^\circ$, in absolute alcoholic solution; the corresponding di-acetate has m. p. 150° , $[\alpha]_D^{25} + 76.47^\circ$, when dissolved in chloroform. *Hederagenin methyl ester* is converted by fuming nitric acid into a nitro-compound, decomp. 165° , which has not been analysed. The gradual addition of a solution of bromine in chloroform to hederagenin methyl ester dissolved in the same solvent leads to the formation of the dibromo-compound, $\text{C}_{32}\text{H}_{50}\text{O}_4\text{Br}_2$, small, colourless needles, decomp. $215-217^\circ$. Bromination of hederagenin under similar conditions appears to proceed somewhat irregularly, giving on the one hand a bromo-derivative, colourless needles, decomp. $157-158^\circ$, which was not analysed but is probably a dibromo-compound (Tamburello), and, on the other, a mixture of two bromo-derivatives, lustrous, hexagonal leaflets, m. p. 242° , and pale yellow needles, $\text{C}_{31}\text{H}_{48}\text{O}_4\text{Br}_2$, m. p. 262° (van der Haar); attempts to repeat the latter preparations led, however, to somewhat different results, giving products of m. p. $268-270^\circ$ and 255° , respectively.

Hederagenin acid amide, $\text{C}_{31}\text{H}_{51}\text{O}_3\text{N}\cdot\text{H}_2\text{O}$, colourless needles, m. p. 285° , is prepared by the action of ammonia on an ethereal solution of the corresponding chloride obtained by the action of thionyl chloride on hederagenin or its sodium salt. H. W.

Picrotoxin. XII. Picrotin Ketone, $\text{C}_{14}\text{H}_{16}\text{O}_3$. PAUL HORMANN and FRIEDRICH BISCHOF (*Arch. Pharm.*, 1921, **259**, 165-176).—The ketone, $\text{C}_{14}\text{H}_{16}\text{O}_3$, first noticed among the reduction products of picrotoxin by phosphorus and hydriodic acid by Angelico (A., 1910, i, 577) was obtained in better yield by first converting the picrotoxin into α -picrotinic acid and picrotoxinic acid by boiling with mineral acid, and then reducing these acids in the same way as picrotoxin itself. It was isolated by means of its oxime, m. p. 212° , and purified by distillation in a vacuum, b. p. $190^\circ/8$ mm. It forms a thick, colourless syrup which crystallises after long keeping. Its *semicarbazone* has m. p. 216° . By the action of methyl alcoholic potassium hydroxide it is hydrolysed into acetic acid and the substance $\text{C}_{12}\text{H}_{14}\text{O}_2$. An attempted degradation of the ketone by converting it into an unsaturated compound through the corresponding tertiary alcohol obtained by the action of magnesium methyl iodide was not successful. *Oziminopicrotin ketone*, $\text{C}_{11}\text{H}_{11}\text{O}_2\cdot\text{C}(\text{NOH})\cdot\text{COMe}$ is obtained by the

action of amyl nitrite and sodium ethoxide on the ketone. It is a white substance, m. p. 215° , and forms a *semicarbazone*, m. p. 249° (decomp.), a *phenylhydrazone*, m. p. 220° , an *oxime*, m. p. 192° , and a benzoyl derivative, m. p. $178-182^{\circ}$. It did not yield the diketone on treatment with sodium nitrite or mineral acids, but on oxidation with nitric acid or ammoniacal silver oxide it was converted into acetic acid and a *monobasic acid*, $C_{11}H_{11}O_2 \cdot CO_2H$, which could not be obtained in a crystalline condition. By the action of sodium hypobromite, the ketone was converted into α -*bromopicrotin ketone*, $C_{14}H_{15}O_3Br$, coarse needles, m. p. 145° .
G. F. M.

Physiology of Anthocyanin and Chemistry of Chlorophyll. J. COSTANTIN (*Ann. Sci. Nat. Bot.*, 1919, [x], 1, 38-52).—A discussion of the present state of knowledge with regard to anthocyanin and chlorophyll. Reduction with nascent hydrogen of a yellow flavone pigment from *Vitis* is known to yield anthocyanin, and the production of a yellow flavone by oxidation of anthocyanin is affirmed. Chlorophyll is now considered to have the formula $CO_2H \cdot C_{31}H_{29}N_4Mg(CO_2Me)(CO_2 \cdot C_{20}H_{39})$. Treatment with ethyl alcohol produces substitution of an ethyl group for the phytol group, $C_{20}H_{39}$, yielding Willstätter's crystallisable chlorophyll.

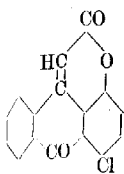
CHEMICAL ABSTRACTS.

Catechutannins. I. Paullinia Tannin. MAXIMILIAN NIERENSTEIN (*T.*, 1922, 121, 23-28).

Anthracoumarin Derivatives. I. W. J. MINAEFF and KURT RIPPER (*Monatsh.*, 1921, 42, 73-81).—The only derivatives of anthracoumarin (Kostanecki, A., 1888, 291) as yet known are styrogallol (Jakobson and Julius, A., 1888, 56; Kostanecki, A., 1888, 292) and a hydroxystyrogallol (Slama, A., 1900, i, 177), which are both mordant dyestuffs. In order to obtain compounds with structures similar to those of the vat dyestuffs derived from anthraquinone, the authors have synthesised 6-chloroanthracoumarin, which has been converted into 1-anilinoanthracoumarin. Preliminary experiments on the preparation of di-anthracoumaryl have also been carried out.

The 6-chloro-3-hydroxybenzoic acid required was prepared (1) by Mazzara and Bertozzi's method (A., 1900, i, 596), (2) by Peratoner and Condorelli's method (A., 1898, i, 642), with the difference that the hydroxyl of the 6-chloro-3-hydroxytoluene was protected during the oxidation by formation of the monophosphoric ester (Heymann and Koenigs, A., 1887, 241), and (3) by reduction of 6-chloro-3-nitrobenzoic acid (Holleman and de Bruyn, A., 1901, i, 591), followed by replacement of the resulting amino-group by hydroxyl.

Condensation of cinnamic and 6-chloro-3-hydroxybenzoic acids in presence of sulphuric acid yields 1-chloroanthracoumarin, which resembles 1-chloroanthraquinone in chemical behaviour, except that its chlorine is more mobile, probably owing to the influence of the negative radicle in the para-position.



6-Chloroanthracoumarin (annexed formula) sublimates in long, golden needles and crystallises in a felted mass of golden needles, m. p. 274°.

6-Anilinoanthracoumarin, $C_{22}H_{13}O_3N$, prepared from 1-chloroanthracoumarin and aniline in presence of fused potassium acetate and copper acetate, crystallises in reddish-violet leaflets, m. p. 184—186°.

The interaction of 6-chloroanthracoumarin and nitrobenzene in presence of "Naturkupper C" appears to yield 6-anthracoumaryl, but no pure product was isolated. T. H. P.

Phenylthioxanthyl. M. GOMBERG and WESLEY MINNIS (*J. Amer. Chem. Soc.*, 1921, **43**, 1940—1944).—The work of Gomberg and Schoepfle (cf. A., 1917, i, 551) on the molecular weight of phenylxanthyl checked by parallel oxygen absorptions has been extended to phenylthioxanthyl. Pure phenylthioxanthanol chloride was prepared by bubbling dry air through a solution of phenylquinothioxanthanol chloride hydrochloride in dry benzene at 90°. This material was used for the oxygen absorption and for the attempts to prepare the free radicle. The free radicle was prepared in solution, but found to be very unstable, and it could not be isolated in the solid state. The values obtained by Schlenck and Renning (cf. A., 1913, i, 34) for the molecular weight of this substance were made on material which was, in all probability, not the free radicle. W. G.

2:2'-Sulphonidotriphenylmethyl. M. GOMBERG and E. C. BRITTON (*J. Amer. Chem. Soc.*, 1921, **43**, 1945—1950).—2:2'-sulphonidotriphenylcarbinol, $HO-CPh<\overset{C_6H_4}{C_6H_4}>SO_2$, m. p. 224—225°, was obtained by the oxidation of phenylthioxanthanol or by the action of magnesium phenyl bromide on benzophenone sulphone. When heated with phosphorus pentachloride at 110—120°, it yielded 2:2'-sulphonidotriphenylcarbonyl chloride, m. p. 160—161°, which, when reduced with stannous chloride and hydrochloric acid, gave 2:2'-sulphonidotriphenylmethane, m. p. 193—194°. The carbonyl chloride when shaken in benzene solution with molecular silver gave the free radicle, 2:2'-sulphonidotriphenylmethyl, m. p. 180° (decomp.), which when exposed in benzene solution to air yielded a crystalline peroxide, m. p. 238—239° (decomp.).

The oxygen and iodine absorptions of the free radicle were determined, and molecular-weight determinations in benzene and in *p*-bromotoluene as solvents indicate little change in molecular weight with rise in temperature from 6° to 27°. The free radicle in solution is unimolecular to the extent of 30% to 38%. W. G.

The Anhalonium Alkaloids. II. Constitution of Pellotine, Anhalonidine, and Anhalamine. ERNST SPÄTH (*Monatsh.*, 1921, **42**, 97—115).—If pellotine actually possesses the constitution suggested (A., 1919, i, 548), protection of its phenolic hydroxyl

group by introduction of a carbethoxyl or an ethyl radicle and cautious oxidation of the resulting compound by means of permanganate should yield substituted gallic acids. No trace of the latter could, however, be obtained and similar failure to detect trimethylgallic acid was experienced on oxidising a methylated anhalamine. The view that pellotine and anhalonidine are derivatives of mezcaline containing a phenolic hydroxyl group cannot be maintained, as it is found that dimethylmezcaline methiodide is identical with neither methylpellotine methiodide nor dimethylanhalonidine methiodide.

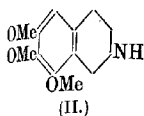
These results suggest that the nitrogen in the two bases forms part of a closed ring, and this view is confirmed by the observation that, when heated with alkali hydroxide, the quaternary, completely methylated pellotine methiodide gives an amine which, when again combined with methyl iodide and subsequently boiled with alkali hydroxide, is converted into a nitrogen-free compound. On the assumptions that the ring in question is the isoquinoline ring, that Heffter's formula, $C_{13}H_{19}O_3N$, for pellotine is correct, and that the base contains a phenolic hydroxyl group, a methyl group united to nitrogen, and a gallic acid residuc, various constitutions are suggested for pellotine methyl ether; the most probable of these is 6:7:8-trimethoxy-1:2-dimethyl-1:2:3:4-tetrahydroisoquinoline, which best expresses the relationship of pellotine to mezcaline and explains the optical inactivity of pellotine, the formation of the latter from mezcaline being brought about by ring closure by means of acetaldehyde, so that assumption of enzyme action is unnecessary. The methiodide of 6:7:8-trimethoxy-1:2-dimethyl-1:2:3:4-tetrahydroisoquinoline, prepared synthetically from mezcaline, is identical with methylpellotine methiodide, and since pellotine contains a hydroxyl group in place of a methoxyl group of the synthetic base, Heffter's formula, $C_{13}H_{19}O_3N$, for pellotine is confirmed.

The identity of the methiodides of the completely methylated derivatives of pellotine and anhalonidine shows that these two bases have the same ring system. Further, the formation of *N*-acyl derivatives of anhalonidine demonstrates the latter to be a secondary base, so that *O*-methylanhalonidine should have the annexed constitution (I), which accords with the observation that the *N*-*m*-nitrobenzoyl derivative of the synthetic base (I) is identical with methyl-*N*-*m*-nitrobenzoyl-anhalonidine; the formula for anhalonidine is, therefore, $C_{12}H_{17}O_3N$, and not, as Heffter thought, $C_{12}H_{15}O_3N$. Thus, pellotine and anhalonidine are derivatives of 6:7:8-trimethoxy-1-methyltetrahydroisoquinoline, but which of the three methoxy-groups exists as hydroxyl in the original bases remains undecided.

As regards anhalamine, it appeared possible that this represents *N*-methylmezcaline with a hydroxyl in place of one of the methoxy-groups. The non-identity of the methiodides of dimethylmezcaline and dimethylanhalamine shows, however, that anhalamine is not



of the mezcaline type, and the further observation that O-methylanhalamine fails to yield the trimethyl ether of gallic acid when oxidised proves that the nitrogen atom does not occur in an open side-chain and indicates that this compound may be



an isoquinoline derivative of the structure (II). The accuracy of the latter is proved by the facts that this compound is readily synthesised from mezcaline and formaldehyde and that it gives an N-m-nitrobenzoyl derivative identical with N-m-nitrobenzoyl-O-methylanhalamine; further, the quaternary iodides of the base (II) and O-methylanhalamine are identical. Anhalamine is therefore the dimethyl-ether of 6 : 7 : 8-trihydroxytetrahydroisoquinoline, but here also the position of the non-methylated phenolic hydroxyl is unknown. Heffter's formula, $C_{11}H_{15}O_3N$, for anhalamine is thus confirmed.

Of the anhalonium alkaloids, anhaline and mezcaline belong to the β -phenylethylamines occurring in various plant families, and are almost certainly decomposition products of substituted phenylalanines resulting from the degradation of proteins. The presence in the same plants as anhaline and mezcaline of the tetrahydroisoquinoline derivatives, pellotine, anhalonidine, and anhalamine, indicates that the latter are formed from the former by condensation with acetaldehyde or formaldehyde.

6 : 7 : 8-Trimethoxy-1-methyl-3 : 4-dihydroisoquinoline, obtained by the action of phosphoric oxide on the N-acetyl derivative of synthetic mezcaline, yields a *picrate*, $C_{13}H_{17}O_3N_3C_6H_3O_7N_3$, m. p. 181—182°; a *platinichloride*, $(C_{13}H_{17}O_3N)_2 \cdot H_2PtCl_6$, which forms orange crystals darkening at 199°, m. p. 200—201° (frothing), and an *aurchloride*, $C_{13}H_{17}O_3N \cdot HAuCl_4$, which forms straw-yellow crystals, m. p. 154—156°.

6 : 7 : 8-Trimethoxy-1-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline, formed from the preceding compound by catalytic hydrogenation in presence of platinum and palladium, yields a *picrate*, $C_{13}H_{19}O_3N \cdot C_6H_3O_7N_3$, m. p. 172—173°, a *platinichloride*, $(C_{13}H_{19}O_3N)_2 \cdot H_2PtCl_6$,

m. p. on slow heating 204—206° (decomp.), on rapid heating 210—212°; and an *aurchloride*, m. p. 147—148° (frothing). The action of methyl sulphate on this base gives

6 : 7 : 8-Trimethoxy-1 : 2-dimethyl-1 : 2 : 3 : 4-tetrahydroisoquinoline, which is identical with methylpellotine and forms a *picrate*, $C_{15}H_{23}O_3N \cdot C_6H_3O_7N_3$, m. p. 167—168°, an *aurchloride*, m. p. 135—136°, and a *platinichloride*, m. p. 216—217° (decomp.).

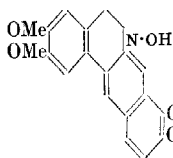
Dimethylanhalamine methiodide, $C_{14}H_{22}O_3NI$, forms crystals, m. p. 211.5—212.5°.

6 : 7 : 8-Trimethoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline, prepared from mezcaline and formaldehyde according to Decker and Becker's process (A., 1913, i, 291), forms a *hydrochloride*, $C_{13}H_{17}O_3N \cdot HCl$, m. p. 242—243°, an *aurchloride*, m. p. 139—140° (frothing), a *platinichloride*, m. p. 207—208° (frothing and blackening), and a *picrate*, m. p. 184—185°; the quaternary iodide, obtained by treating the hydrochloride with methyl sulphate and sodium

hydroxide and subsequently with sodium iodide, is identical with dimethylanhalamine methiodide (*vide supra*).

N-m-Nitrobenzoylanhalamine, $C_{16}H_{12}O_4N_2(OMe)_2$, has m. p. 175–176°, and its methyl ether, $C_{16}H_{11}O_3N_2(OMe)_3$, m. p. 147–148°. T. H. P.

Conversion of Berberine into Palmatine. ERNST SPÄTH and NORBERT LANG (*Ber.*, 1921, 54, [B], 3064–3074).—Palmatine



has been isolated from calumba root by Feist (A., 1908, i, 101) and, subsequently, the annexed formula has been assigned to it by Feist and Sandstedt (*Arch. Pharm.*, 1918, 256, 1). The close similarity of this formula to that of berberine has induced the authors to attempt to confirm it by direct synthesis. For this purpose, bromopapaverine was reduced by granulated tin and hydrochloric acid to tetrahydrobromopapaverine, m. p. 111° (+xH₂O), m. p. 71–73°, which was treated with a mixture of glacial acetic acid, hydrochloric acid, water, and methylal. A small amount of a product, m. p. 151–153°, was thus obtained which was possibly bromotetrahydropalmatine. Debromination of this substance by hydrogen in the presence of palladised barium sulphate did not yield tetrahydropalmatine but norcoralydine (cf. Pictet and Tsau Quo Chou, A., 1916, i, 418).

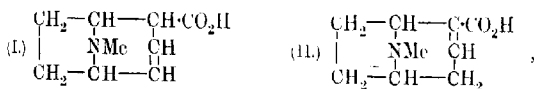
The possibility of removing the hydroxymethylene group of berberine and replacing it by two methoxyl groups (thus giving palmatine) has been examined. Orientating experiments with piperonal and tetrahydroberberine showed that the hydroxymethylene group can be removed with some difficulty by dilute hydrochloric acid under suitable conditions, but, simultaneously, the phenol produced is very extensively resinified by the liberated formaldehyde. Better results were obtained with tetrahydroberberine and methyl alcoholic potassium hydroxide solution in an evacuated tube at 180°; it is remarkable that, under suitably chosen conditions, the hydroxymethylene group can be removed, whereas the two methoxyl groups remain intact. Nuclear condensation by the liberated formaldehyde appears to occur to only a slight extent, probably owing to the rapid transformation of the aldehyde into potassium formate and methyl alcohol. Methylation of the product of the change by diazomethane gave a poor yield of tetrahydropalmatine. Better results were obtained by its complete methylation by treatment with a large excess of methyl sulphate and alkali in the absence of oxygen and isolation of the completely methylated quaternary iodide by addition of potassium iodide and potassium hydroxide. The salt was found to be identical with tetrahydropalmatine methiodide. When distilled in a vacuum, it gave tetrahydropalmatine, identical with the product derived from natural sources. It was oxidised by a solution of iodine in alcohol to palmatine.

H. W.

A New Base from the Residues of the Hydrolytic Products of Cocaine, Isomeric with Tropine and ψ -Tropine. J. TRÖGER and K. SCHWARZENBERG (*Arch. Pharm.*, 1921, **259**, 207—226).—By fractional crystallisation from alcohol of the hydrochlorides of the basic residues left after the removal of the ecgonine from the product of the hydrolysis of the coca alkaloids, the hydrochloride of a new base, isomeric with tropine and ψ -tropine, was isolated from the more soluble fractions. The new base, $C_8H_{15}ON$, is a very hygroscopic, crystalline substance, m. p. 53° , b. p. 225 — 230° , and distinctly volatile at the ordinary temperature. The *hydrochloride*, *hydrobromide*, and *hydriodide* are crystalline salts, very soluble in water and alcohol, and melt at 157 — 160° , 175° , and 186° , respectively. The *picrate*, $C_8H_{15}ON \cdot C_6H_3(NO_2)_3 \cdot OH$, forms hygroscopic, yellow needles, which sinter at 225° , and decompose at 237° . The *platinichloride*, $(C_8H_{15}ON)_2 \cdot H_2PtCl_6$, is also very soluble in water, and was obtained in long, yellow needles, m. p. 184° , by evaporating the aqueous solution to dryness and crystallising from absolute alcohol and ether. The preparation of the aurichloride in an analytically pure state presented difficulties owing apparently to partial reduction and varying gold content of the salt. The *benzoyl* derivative, crystallised from a mixture of alcohol and ether, formed glistening, white prisms, m. p. 139 — 140° . The *methiodide* of the base crystallises from alcohol in well characterised, white needles, m. p. 238 — 240° . It was converted into the corresponding ammonium base by means of silver oxide, and this on distillation gave trimethylamine and a residue giving no solid derivatives and otherwise not further examined. Attempts to oxidise the original base with chromic acid, permanganate, ferricyanide, and hydrogen peroxide were either without result or gave oily products from which solid derivatives could only in one or two instances be obtained, and then not in an analytically pure condition.

G. F. M.

Ecgonine. LXIX. J. GADAMER and CARL JOHN (*Arch. Pharm.*, 1921, **259**, 227—240).—Of the two possible formulæ for anhydroecgonine,



Willstätter decided in favour of I (A., 1899, i, 178), but it is now shown that formula II must be correct, since on reduction to hydroecgonidine at least two different optical isomerides are produced, which could only be the case by the creation of a third asymmetric carbon atom, and on the basis of formula I this is not possible without assuming the occurrence of isomerisation during the reduction. Such isomerisation is conceivable if the reduction is carried out by Willstätter's method with sodium and amyl alcohol, but the hydrogenation was also carried out by the Paal and Skita method, in which an isomerisation is extremely unlikely, and two

sulphuric acid to a mixture of α -methyltetrahydropalmatine^s, greenish-yellow leaflets, m. p. 165° and m. p. 67—69°, respectively.

H. W.

Codeineoxidesulphonic Acids and their Derivatives.

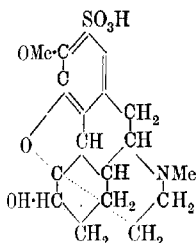
EDMUND SPEYER and HERMANN WIETERS (*Ber.*, 1921, **54**, [B], 2976—2987).—The action of acetic anhydride and sulphuric acid on codeine-*N*-oxide has been shown by Freund and Speyer (*A.*, 1911, i, 809) to lead to the formation of α -codeine-*N*-oxidesulphonic acid, $C_{18}H_{20}O_3 \leq \begin{smallmatrix} SO_2 \\ N(OH) \end{smallmatrix} > O$, and codeine-*N*-oxidesulphonic

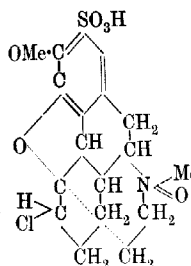
acid, $C_{18}H_{20}O_3 \leq \begin{smallmatrix} SO_3H \\ N:O \end{smallmatrix}$, which are reduced by sulphurous acid to the same codeinesulphonic acid. The behaviour of the isomeric sulphonic acids when catalytically hydrogenated is now described.

Codeine-*N*-oxidesulphonic acid is reduced by hydrogen in the presence of colloidal palladium to *dihydrocodeinesulphonic acid* (annexed formula), six-sided leaflets or well-defined prisms, decomp. 330—340° after darkening at 30°, $[\alpha]_D^{20} -76.7^\circ$ in faintly alkaline solution. The same acid is obtained by catalytic hydrogenation of codeinesulphonic acid. The acid is reconverted by water at 150° or by stannous chloride and concentrated hydrochloric acid at 100° into dihydrocodeine. It is transformed by nitric acid (*d* 1.36) into nitrodihydrocodeine, yellow double pyramids, m. p. 221°, identical with the substance described by Freund and Melber (*A.*, 1920, i, 717). Similarly, α -codeineoxidesulphonic acid yields α -*dihydrocodeinesulphonic acid*, a colourless, crystalline powder, decomp. 315—320°, $[\alpha]_D^{20} -88^\circ$ in aqueous solution; the corresponding *monohydrate* is also described. It is converted by water at 150—160° into dihydrocodeine and by cold nitric acid (*d* 1.36) into α -*nitrodihydrocodeine*, slender, yellow needles, m. p. 180°.

Attempts were also made to prepare the isomeric dihydrocodeine-sulphonic acid from dihydrocodeine. For this purpose, the latter was transformed by hydrogen peroxide into *dihydrocodeine-N-oxide*, pale yellow, rhombic crystals, decomp. 225° after softening at 215° (*hydrochloride*, hexagonal plates, m. p. 217° after previous softening; *picrate*, four-sided prisms, m. p. 161—162°). Under the action of sulphuric acid and acetic anhydride, the latter yields a single *dihydrocodeine-N-oxidesulphonic acid*, $C_{18}H_{23}O_3NS$, prisms, decomp. 273—275°, which is reduced by sulphurous acid to dihydrocodeine-sulphonic acid.

The applicability of sulphoacetic acid for the sulphonation of derivatives of codeine has been tested further in the case of chlorodihydrocodeine-*N*-oxide (cf. Freund and Melber, *loc. cit.*). It has been found possible to isolate a *chlorodihydrocodeine-N-oxidesulphonic*





acid (annexed formula), feathery crystals, decomp. 290—295°, but the occurrence of an isomeride could not be observed. The acid is reduced by sulphurous acid to *chlorodihydrocodeinesulphonic acid*, prisms, decomp. about 300°.

Dihydrocodeinesulphonic acid, after neutralisation by sodium hydroxide, is converted by an excess of methyl iodide into *dihydrocodeinesulphonic acid methylhydroxide*, $C_{19}H_{27}O_4NS$, rectangular plates, decomp. 280—285°; the latter is very stable towards water, but is decomposed by sodium hydroxide solution (4%) at 140° into tetramethylethylenediamine and a nitrogen-free substance which could not be isolated.

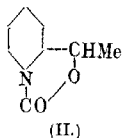
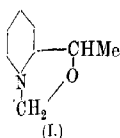
In view of the mutability of the codeine molecule, it is possible that the formation of isomeric sulphonic acids is due to preliminary isomerisation of the codeine itself. In this case, it must be possible to derive one of the sulphonic acids from an isomeric codeine. In this connexion, ψ -codeine has been transformed by hydrogen peroxide into ψ -codeine-*N*-oxides, prisms, m. p. 226—228° (*picrate*, needles, m. p. 166—168°), which is transformed by a mixture of acetic anhydride and sulphuric acid into ψ -codeine-*N*-oxidesulphonic acid, long, glassy prisms, decomp. about 300°, which is not identical with α -codeineoxidesulphonic acid, although resembling it in being soluble in water.

H. W.

1- α -N-Methylpiperidylethane-1-one. KURT HESS and WILHELM CORLEIS (*Ber.*, 1921, 54, [B], 3010—3020).—The synthesis of 1- α -N-methylpiperidylethane-1-one is described, the method adopted being similar to that used in the preparation of the corresponding propane derivative, which the new substance resembles closely. Unexpectedly, its transformation into hygrine could not be realised on account of the failure to effect demethylation to the secondary amine.

α -Pyridyl methyl ketone is catalytically hydrogenated in the presence of platinum to a mixture of the diastereoisomeric forms of 1- α -piperidylethane-1-ol, b. p. 106—110°/18 mm., which is converted by formaldehyde and formic acid into a mixture of 1- α -N-methylpiperidylethane- α -ols, b. p. 91—105°/22 mm. The latter is oxidised by chromic acid in acetic acid solution to 1- α -N-methylpiperidylethane- α -one, $C_8H_{15}NMe \cdot COMe$, a mobile, hygroscopic liquid, b. p. 78—80°/14 mm., which decomposes somewhat rapidly when preserved. The *picrate*, short prisms, m. p. 119—120°, *semicarbazone*, m. p. 175—177°, *methiodide*, small plates, m. p. 144°, and a non-homogeneous *hydrazone*, b. p. 115—117°/15 mm. [*picrate* of latter, m. p. 189° (decomp.)], are described. The hydrazone is converted by a solution of sodium ethoxide in alcohol at 160—170° into 1- α -N-methylpiperidylethane (*picrate*, m. p. 170—171°). The ketone does not react with ethyl azidodicarboxylate. It reacts

with cyanogen bromide to form the expected methobromide (*aureochloride* of the corresponding *methochloride*, $C_9H_{18}ONCl \cdot AuCl_3$, ochre-yellow crystals, m. p. 142°) and cyanamide derivative, but the hydrolysis of the latter leads to the production of a non-basic substance (which was not obtained in the pure state, but is probably an imidazolone derivative) in place of the desired secondary ketone.



The action of formaldehyde and hydrochloric acid on 1- α -piperidylethane-1-ol at $120-130^\circ$ leads to the production of the *oxazolidine* derivative (annexed formula I), b. p. $79-81^\circ/18$ mm. (*picrate*, slender needles, m. p. 163°), whereas the corresponding *oxazolide* (annexed formula II), b. p. $164^\circ/14$ mm., is obtained when the urethane of 1- α -piperidylethane- α -ol is distilled under diminished pressure.

H. W.

The Preparation of Pyridine and of certain of its Homologues in a State of Purity. JOSEPH GREENWOOD HEAP, WILLIAM JACOB JONES, and JOHN BAMBER SPEAKMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 1936—1940).—Pyridine, 2-methylpyridine, and 3-methylpyridine were separated from the crude coal tar bases from a light oil by repeated fractional distillation and subsequently purified through their additive compounds with zinc chloride. 2:6- and 2:4-Dimethylpyridines were similarly obtained from the crude bases of middle oil, but purified through their mercurichlorides. The following physical constants, using special precautions, were obtained: pyridine, b. p. 115.3° ; d_4^{20} 0.9776; 2-methylpyridine, b. p. $128-129^\circ$; d_4^{20} 0.9404; 3-methylpyridine, b. p. 143.8° ; d_4^{20} 0.9515; 2:6-dimethylpyridine, b. p. 137.5° ; d_4^{20} 0.9200; 2:4-dimethylpyridine, b. p. 157.1° ; d_4^{20} 0.9273.

W. G.

Some Physical Properties of Aqueous Solutions of certain Pyridine Bases. WILLIAM JACOB JONES and JOHN BAMBER SPEAKMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 1867—1870; compare preceding abstract).—The densities of aqueous solutions of pyridine, 2-methylpyridine, and 3-methylpyridine have been determined at 25° . In the case of pyridine, the density rises with increasing concentration of water, to a maximum (1.0032) at 50% water; in the other cases the density rises regularly with increasing concentration of water. The composition of the constant boiling mixture of each of the three bases is determined at various pressures, and it is shown that at ordinary pressures the constant boiling mixture with pyridine contains 42% of water, with 2-methylpyridine 48% of water, and with 3-methylpyridine 61% of water. The boiling points of the mixtures are respectively, 93.0° , 93.5° , and 96.2° . The miscibility of 2:4-dimethylpyridine with water has been investigated. It is shown that the minimum critical solution temperature is 22.5° ,

and the boiling point of the constant boiling mixture is 96.5°. The distillate condensed into two layers, but on cooling below 23.2° it became homogeneous and contained 66% of water.

J. F. S.

5-Methoxydioxindole and 5-Methoxyisatin. J. HALBERKANN (*Ber.*, 1921, **54**, [B], 3079—3090; cf. this vol., i, 174).—The experiments described were undertaken in the hope of discovering a convenient method for the preparation of quinic acid in quantity; they were not completely successful.

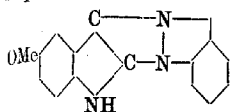
Ethyl mesoxalate condenses with *p*-anisidine in hot glacial acetic acid solution to give *ethyl 3-hydroxy-5-methoxy-2-ketodihydroindole-*

3-carboxylate, $\text{NH}\cdot\text{C}_6\text{H}_3\cdot\text{OMe}$
 $\text{CO}\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{Et}$, coarse, colourless needles or plates,

m. p. 193—194°. The yield is 33—37% of that theoretically possible, and is not improved by the addition of anhydrous sodium acetate or of acetic anhydride. A *by-product*, brownish-yellow, rectangular platelets or needles, m. p. 256°, is also formed. The ester is not produced when its components are melted together. It is converted by acetic anhydride and sodium acetate into the corresponding *diacetyl* compound, colourless rhombohedra, m. p. 122—123°, and by a large excess of phenylhydrazine or hydroxylamine into 5-methoxyisatin-3-phenylhydrazone, m. p. 216—217° (Bauer, A., 1909, i, 467, gives m. p. 219°), and 5-methoxyisatin-3-*oxime*, brownish-red, intertwined, prismatic needles, m. p. 234—235°. Hydrolysis of the ester with potassium hydroxide, and subsequent acidification with hydrochloric acid leads to the separation of 5-methoxydioxindole, long, colourless to pale brown, four-sided needles, m. p. 204—205° [*diacetyl* compound, colourless, rhombohedric prisms, m. p. 225—226° (decomp.).] When an ice-cold solution of the dioxindole in alkali is acidified with acetic acid, 2-amino-5-methoxymandelic acid, colourless plates or rhombohedra (+1H₂O) separates. It has m. p. 160—161° (evolution of steam) when heated rapidly, after which it resolidifies and melts again at 203—204° (m. p. of 5-methoxydioxindole). An aqueous suspension of the acid is coloured brown, green, bluish-violet, and ultimately dark red by ferric chloride; the action does not depend on complex salt formation, since a similar effect is produced by bromine water. A diazotised solution of the acid couples with an alkaline solution of β -naphthol to give a dark reddish-violet dye. The stability of the acid is remarkable, since *o*-aminomandelic acid appears to be incapable of existence.

5-Methoxydioxindole is only converted with difficulty by air or oxygen into 5-methoxyisatin; as a rule, the action only proceeds to the formation of the *methoxylated isatyde*, m. p. 246° (decomp.) after softening at 135° (? water of crystallisation). 5-Methoxyisatin, almost black, prismatic needles, is, however, readily produced from the dioxindole by the action of very dilute ferric chloride solution. When boiled with an alcoholic solution of aniline, 5-methoxyisatin yields the corresponding 3-anilide, lustrous, orange-red needles, m. p. 223°, which dissolves to a dark green solution in concentrated

sulphuric acid. The acetyl



needles when heated cautiously.

derivative of 5-methoxyisatin forms red, prismatic needles or coarse prisms, m. p. 144–145°. When the isatin is melted with *o*-phenylenediamine, it gives 10-methoxyindophenazine (annexed formula), m. p. 247°, which sublimes in long, orange-yellow

H. W.

Bromo-2-methylquinolines. K. L. MOUDGILL (*J. Amer. Chem. Soc.*, 1921, **43**, 2257–2258).—6-Bromo-2-methylquinoline is prepared by the condensation of *p*-bromoaniline and paracetaldehyde in hydrochloric acid (cf. Bastow and MacCollum, *A.*, 1904, i, 686). It gives a *methiodide*, m. p. 237° (decomp.), and an *ethiodide*, m. p. 218°. *m*-Bromoaniline condenses with paracetaldehyde to give (?) *bromo-2-methylquinoline*, m. p. 77°, giving an *ethiodide*, m. p. 217°; a *nitrate*, m. p. 102°; a *zincchloride*, m. p. 268°; a *stannichloride*; a *mercurichloride*, m. p. 245°; and a *picrate*, m. p. 207°. Whether the bromine atom is in position 5 or 7 has not been settled.

W. G.

Constitution of Kynurenic Acid. ERNST SPÄTH (*Monatsh.*, 1921, **42**, 89–95).—Kynurenic acid, regarded by Camps (*A.*, 1901, i, 751) as 4-hydroxyquinoline-3-carboxylic acid, was shown by Homer (*A.*, 1914, i, 730) to have m. p. 289°, which is that of the 4-hydroxyquinoline-2-carboxylic acid obtained by Camps. Neither Camps nor Homer, however, compared derivatives of natural kynurenic acid with those of the synthetic hydroxyquinolinecarboxylic acid, and Ellinger and Matsuoka's work (*A.*, 1920, i, 696) on the conversion of tryptophan into kynurenic acid in the animal body appears to indicate the accuracy of Camps's constitution for the acid.

The author finds that kynurenic acid may be rapidly freed from protein compounds by conversion into its methyl ester, the hydrochloride of which is sparingly soluble in methyl alcohol. Treatment of the pure kynurenic acid with phosphorus pentachloride yields a 4-chloroquinolinecarboxylic acid and catalytic replacement of the chlorine by hydrogen in presence of palladium and barium sulphate yields quinoline-2-carboxylic acid, which was identified by means of its methyl ester and amide. Further, the methyl ester, the methyl ester of the methyl ether, and the benzoyl-methyl ester of synthetic 4-hydroxyquinoline-2-carboxylic acid agree in properties with the corresponding derivatives of natural kynurenic acid. The contradictory results of Camps and Homer appear to be due to the fact that the melting point of kynurenic acid varies from 255° to 289°, according to the rapidity of the heating.

Methyl kynurenate methyl ether (methyl 4-methoxyquinoline-2-carboxylate), $C_{12}H_{11}O_3N$, has m. p. 148–149°, and *methyl benzoyl-kynurenate*, $C_{18}H_{13}O_4N$, forms white crystals, m. p. 143°.

T. H. P.

g*

Derivatives of Quinic Acid. J. HALBERKANN (*Ber.*, 1921, 54, [B], 3090—3107).—A record of the preparation of derivatives of quinic acid from 5-methoxyisatin (cf. Halberkann, this vol., i, 172).

5-Methoxyisatin condenses with pyruvic acid in alkaline solution to form 6-methoxyquinoline-2:4-dicarboxylic acid, almost colourless, prismatic rods or prisms, m. p. 239—240° (evolution of carbon dioxide). The lead, copper, silver, and ferric salts were prepared. When heated with concentrated hydrochloric acid under pressure, the acid is converted into 6-hydroxyquinoline-2:4-dicarboxylic acid, small needles or plates (+1H₂O), m. p. 318°, which couples with diazonium salts in the usual manner. [The ammonium hydrogen salt, needles (+1H₂O), has m. p. 318° (decomp.) after becoming discoloured at 285°.] 5-Methoxyquinoline-2:4-dicarboxylic acid loses carbon dioxide when heated slightly above its melting point and passes into 6-methoxyquinoline-4-carboxylic acid (quinic acid) which is identical with the substance derived from quinine. The direct production of quinic acid from 5-methoxyisatin and acetaldehyde is impossible, since the latter becomes resinified by the alkali, whilst, if acetoxime is used it is difficult to remove the methoxy-β-isatoxime formed simultaneously. Attempts to prepare the acid directly from *p*-anisidine (cf. Pictet and Mesner, A., 1912, i, 650) by replacing the pyruvic ester by the free acid and methylal by ethyl orthoformate, gave only small yields of the desired substance.

6-Methoxyquinoline-2:3:4-tricarboxylic acid, aggregates of needles (+1H₂O), m. p. 224—225° (decomp.) after previous darkening, is prepared by the condensation of 5-methoxyisatin and ethyl oxalacetate in concentrated alkaline solution. 5-Methoxyisatin and acetophenone in hot alcoholic alkaline solution give 6-methoxy-2-phenylquinoline-4-carboxylic acid, pale yellow needles (+1H₂O), m. p. 236°, which, however, is prepared more conveniently from *p*-anisidine, benzaldehyde, and pyruvic acid. When triturated with hydrochloric acid (*d* 1.125), the acid gives an intensely yellow hydrochloride which is decomposed readily by water. When heated with concentrated hydrochloric acid under pressure, the methoxyacid is converted into 6-hydroxy-2-phenylquinoline-4-carboxylic acid, yellow needles, m. p. 330° (decomp.). The latter couples with diazotised sulphanilic acid, giving 5-*p*-sulphobenzenazo-6-hydroxy-2-phenylquinoline-4-carboxylic acid, a red, structureless powder which darkens above 200° and gradually becomes carbonised, without melting, at a higher temperature. The corresponding aniline salt, dark red prisms, behaves similarly when heated. The azo-dye is reduced by sodium hyposulphite to 5-amino-6-hydroxy-2-phenylquinoline-4-carboxylic acid, an unstable substance which passes readily into the corresponding quinone.

6-Methoxy-2-phenylquinoline-4-carboxylic acid is smoothly converted by the calculated quantity of potassium nitrate in the presence of concentrated sulphuric acid into 5-nitro-6-methoxy-2-phenylquinoline-4-carboxylic acid, long, pale-yellow, rectangular platelets, m. p. 262° (decomp.), when rapidly heated, after darkening

above 250°. It is reduced by ferrous hydroxide in alkaline solution to 5-amino-6-methoxy-2-phenylquinoline-4-carboxylic acid, rosettes of violet-red needles or platelets, m. p. 255—256° (decomp.). After being diazotised, it couples with β-naphthol in alkaline solution to yield 5-hydroxynaphthaleneazo-6-methoxy-2-phenylquinoline-4-carboxylic acid, almost black, granular aggregates which do not melt below 300°. When the amino-compound reacts in sodium carbonate solution with diazotised sulphanilic acid, it yields 8-p-sulphobenzeneazo-5-hydroxy-6-methoxy-2-phenylquinoline-4-carboxylic acid, a violet powder, m. p. 205° (decomp.) after softening at 190°. According to the author's unpublished observations, a similar replacement of the amino- by the hydroxy-group during coupling is shown by 5-aminohydroquinine.

Deoxybenzoin and 5-methoxyisatin give 6-methoxy-2:3-diphenylquinoline-4-carboxylic acid, colourless needles, m. p. 306° (decomp.). With acetone, 5-methoxyisatin yields 6-methoxy-2-methylquinoline-4-carboxylic acid, bluish-yellow needles, m. p. 286°, which is obtained more conveniently from *p*-anisidine, pyruvic acid, and acetaldehyde. It is converted by concentrated hydrochloric acid at 145° into 6-hydroxy-2-methylquinoline-4-carboxylic acid, slender needles, which begins to decompose above 300° with evolution of a brownish-yellow oil (? 6-hydroxy-2-methylquinoline), but is not completely melted at 340°. The methoxy-acid is converted by chloral into 6-methoxy-2-γ-trichloro-Δ²-propenylquinoline-4-carboxylic acid, colourless, prismatic rods, m. p. 216° (decomp.) after darkening above 190°, which is transformed by alkali into 4-carboxy-6-methoxyquinoline-2-β-acrylic acid, $\text{OMe} \cdot \text{C}_6\text{H}_3 \cdot \text{N} \begin{array}{l} \text{C}(\text{CO}_2\text{H}) \cdot \text{CH} \\ \text{N} \text{-----} \text{C} \cdot \text{CH} \cdot \text{CH} \cdot \text{CO}_2\text{H} \end{array}$, pale

yellow, slender needles, m. p. 249° (decomp.) after darkening at about 220°. The latter is oxidised by potassium permanganate to 6-methoxyquinoline-2:4-dicarboxylic acid.

6-Methoxy-2-(2'-furyl)quinoline-4-carboxylic acid, prepared from 2-acetylfuran and 5-methoxyisatin or from *p*-anisidine, furfuraldehyde, and pyruvic acid, crystallises in yellow needles, m. p. 241° (decomp.) after previous darkening.

1-Acetyl-5-methoxyisatin is quantitatively transformed (apart from the regenerated isatin) when heated with aqueous sodium hydroxide solution into 6-methoxy-2-keto-1:2-dihydroquinoline-4-carboxylic acid, dark yellow, prismatic rods, m. p. 326° (decomp.). When precipitated from its alkaline solution by mineral acids, it forms an almost colourless gel (? 2-hydroxy-6-methoxyquinoline-4-carboxylic acid), which subsequently passes into the yellow variety. The latter does not couple with diazotised sulphanilic acid in sodium carbonate solution. Boiling glacial acetic acid converts that portion of it which remains undissolved into intensely yellow, woolly needles, m. p. 326° (decomp.). The corresponding ethyl ester, small, orange-yellow needles, m. p. 231° after softening at 205°, can be obtained directly in small amount from *p*-anisidine and ethyl oxalacetate in glacial acetic, but not in alcoholic solution.

H. W.

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Influence of Substitution in the Components on Equilibria in Binary Solutions. XXXIII. The Binary Systems of Carbazole or Acenaphthene with Polynitro-derivatives of Benzene and Toluene. ROBERT KREMANN and HUBERT STRZELBA (*Monatsh.*, 1921, 42, 167—180; cf. this vol., i, 159).—The results obtained by Kremann and Slovak (A., 1920, i, 564) show that the ability of picric acid to combine with carbazole depends on its nitro-groups, the hydroxyls being inert.

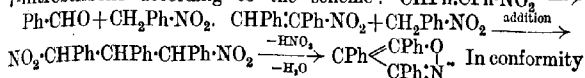
The authors find that no compound is formed in the solid state by carbazole with any one of the three dinitrobenzenes or with 2:4-dinitrotoluene, simple eutectics being obtained in all cases. For *o*-, *m*-, and *p*-dinitrobenzenes and 2:4-dinitrotoluene, these eutectics correspond respectively with 107° and 15%; 72° and 13%; 143° and 34%, and 62° and 11% of carbazole. With *s*-trinitrobenzene (1 mol.), carbazole (1 mol.) forms a compound which melts homogeneously (m. p. 203°) with little dissociation and gives a eutectic with carbazole at 195° containing 44% of trinitrobenzene and a eutectic with trinitrobenzene at 120° containing about 97.5% of trinitrobenzene. With 2:4:6-trinitrotoluene, carbazole also forms a compound (1 mol. : 1 mol.) which, however, exhibits considerable dissociation in the fused condition, so that introduction of the electropositive methyl group appears to weaken the activity of the nitro-groups.

Towards nitro-derivatives of benzene, acenaphthene behaves similarly to naphthalene (Kremann and Haas, A., 1919, ii, 457). With 1:3:5-trinitrobenzene, acenaphthene forms a compound (1 mol. : 1 mol.), m. p. 161°, which with acenaphthene gives a eutectic corresponding with 87° and 8%, and with 1:3:5-trinitrobenzene a eutectic corresponding with 115° and 94% of the trinitrobenzene. With 2:4:6-trinitrotoluene, acenaphthene forms a compound (1 mol. : 1 mol.), m. p. 112° (compare Buguet, A., 1910, i, 105), which gives a eutectic with acenaphthene at 81° containing 18%, and a eutectic with trinitrotoluene at 72° containing 92% of trinitrotoluene. T. H. P.

Triarylisoazoles. JAKOB MEISENHEIMER and KARL WEIBEZAHN (*Ber.*, 1921, 54, [B], 3195—3206).—By the action of potassium hydroxide solution on β -nitro- α -methoxy- $\alpha\beta$ -diphenylethane or on 7-nitrostilbene and as by-product of the condensation of phenylnitromethane with benzaldehyde according to the method of Knoevenagel and Walter (A., 1905, i, 65), Heim (A., 1911, i, 717) has isolated a substance which is regarded as 3:4:5-triphenylisoazazole, $\text{CPh} \begin{smallmatrix} \diagup \text{CPh} \cdot \text{O} \\ \diagdown \text{CPh} \cdot \text{N} \end{smallmatrix}$. The proof of the correctness of this

formula is now given by the observation that the substance is oxidised by ozone to benzoylbenziloxime, $\text{CPh}(\text{N} \cdot \text{OBz})\text{Bz}$; it is remarkable, however, that the benzoyl derivative of benzil β -oxime is produced in place of the expected α -compound (cf. Meisenheimer, this vol., i, 152). The constitution is confirmed further by synthesis of the compound from dibenzoylphenylmethane or tri-benzoylphenylmethane and hydroxylamine. Heim (*loc. cit.*) has

advanced the theory that 3 : 4 : 5-triphenylisooxazole is formed from 7-nitrostilbene according to the scheme: $\text{CHPh:CPh}\cdot\text{NO}_2 \longrightarrow$



with this conception, it is shown that the yields of 3 : 4 : 5-triphenylisooxazole are increased very considerably when an equivalent amount of phenylnitromethane is added to the α -nitrostilbene before it is heated with potassium hydroxide. Further, it is found that α -nitro-4'-methoxystilbene is convertible in good yield into 3 : 5-diphenyl-4-anisylisooxazole, which can only be explained if it is assumed that the nitromethoxystilbene suffers partial fission to anisaldehyde and phenylnitromethane followed by condensation of the latter with unchanged nitromethoxystilbene. Several other substituted isooxazoles have been synthesised in a similar manner. Reaction proceeds smoothly if all three substituents or the two in the 3 and 5 positions are similar. If, however, the two latter are dissimilar, two structural isomerides are generally produced simultaneously. In the latter case, a further complication ensues, owing to the fact that the nitrostilbene suffers fission to the aldehyde and arylnitromethane, the latter not being identical with the arylnitromethane employed. This also condenses with unchanged nitrostilbene, and a complex mixture thus results from which it is impossible to isolate the desired isooxazole.

► 3 : 4 : 5-Triphenylisooxazole, slender, colourless needles, m. p. 212—213°, is stable towards boiling alkaline permanganate and does not absorb bromine. It is converted by boiling nitric acid (d 1.4) into tri-*p*-nitrotriphenylisooxazole, m. p. 298—300°; the simultaneous production of *p*-nitrobenzoic acid shows that the nitro-groups have entered into the *p*-position in the isooxazole compound. α -Nitro-4'-methoxystilbene is converted by boiling sodium hydroxide solution (15%) into 3 : 5-diphenyl-4-anisylisooxazole, colourless, slender needles, m. p. 188—189°.

p-Methoxyphenylacetoneitrile, b. p. 152°/16 mm., is obtained in almost quantitative yield by the action of methyl sulphate and sodium hydroxide on *p*-hydroxyphenylacetoneitrile, and is converted by ethyl nitrate and potassium ethoxide according to the method of Wislicenus and Endres (A., 1903, i, 472) into the potassium salt of *p*-anisylisnitroacetoneitrile, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NO}\cdot\text{OK})\cdot\text{CN}$ (the sodium salt was analysed), which is transformed by boiling sodium hydroxide solution into *p*-anisylnitromethane, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NO}_2$, b. p. 158—160°/11 mm. (the corresponding enolic form, m. p. 65—70°, is unstable). *p*-Anisylnitromethane condenses with benzaldehyde in the presence of a little methylamine to give α -nitro-4-methoxystilbene, $\text{CHPh}\cdot\text{C}(\text{NO}_2)\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, pale yellow crystals, m. p. 95°, and with anisaldehyde to yield α -nitro-4 : 4'-dimethoxystilbene, pale yellow crystals, m. p. 140—141°, b. p. 240—245°/16 mm. α -Nitro-4-methoxystilbene and *p*-anisylnitromethane yield 4-phenyl-3 : 5-di-*p*-anisylisooxazole, colourless needles, m. p. 170—172°. 3 : 4 : 5-Tri-*p*-anisylisooxazole, small, colourless needles,

m. p. 146—147°, is obtained from α -nitro-4:4'-dimethoxystilbene and *p*-anisylnitromethane. Phenylnitromethane and α -nitro-4:4'-dimethoxystilbene give 3(?) 5)-phenyl-4:5(?) 3:4)-di-*p*-anisylisooxazole, colourless needles, m. p. 156—157°. α -Nitrostilbene and α -nitro-4'-methoxystilbene yield with *p*-anisylnitromethane mixtures of isooxazoles from which only the most sparingly soluble components, namely, triphenylisooxazole and 3:5-diphenyl-4-*p*-anisylisooxazole, can be isolated in an approximately homogeneous condition.

An ethereal solution of the sodium compound of deoxybenzoin (prepared by means of sodamide) is converted by benzoyl chloride mainly into tribenzoylphenylmethane, colourless crystals, m. p. 152°. The course of the action is explained by the assumption of the initial formation of dibenzoylphenylmethane which, as a relatively strong acid, displaces the deoxybenzoin from its metallic derivative and forms the sodium compound of the diketone which reacts with a further portion of benzoyl chloride, giving tribenzoylphenylmethane. The latter is converted by hydroxylamine hydrochloride in glacial acetic acid solution in the presence of a little concentrated hydrochloric acid at 200° into 3:4:5-triphenylisooxazole. If the alcoholic solution of the triketone is treated with sodium ethoxide or sodium hydroxide solution at the atmospheric temperature, it passes into dibenzoylphenylmethane, lustrous, pale yellow needles, m. p. (indefinite), 148—151°, after previous softening; the latter can also be prepared, under certain conditions, from sodiodeoxybenzoin and benzoyl chloride. When boiled for a considerable time with a quantity of alcohol insufficient for solution, it is transformed into tribenzoylphenylmethane. It does not appear to be identical with the substance described by Japp and Lander (T., 1896, 69, 742). H. W.

Preparation of Anthraquinone Derivatives [1:2-Anthraquinonylisooxazoles]. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 147001; 160433).—By the action of fuming sulphuric acid on 1-nitro-2-alkyl-anthraquinones or their substitution derivatives, products insoluble in alkalis and of great reactive power are formed, which constitute valuable intermediates for the manufacture of anthraquinone dyes. The substances are produced by the elimination of 1 mol. of water from the nitro-alkylantraquinone, and they are probably isooxazole derivatives of the constitution $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_2 \begin{smallmatrix} N \\ \diagup O \\ \diagdown C-R \end{smallmatrix}$; $\alpha\beta$ -Anthraquinonyl-

isooxazole, prepared by mixing 1 part of 1-nitro-2-methylantraquinone and 20 parts of sand into a paste with 60% fuming sulphuric acid and pouring on to ice, crystallises from xylene as a brownish-yellow powder, sparingly soluble in the usual organic solvents, and melting at 250° (decomp.). 7-Nitro- $\alpha\beta$ -anthraquinonylisooxazole, prepared by introducing 1 part of 1:5-dinitro-2-methylantraquinone into 15 parts of 40% fuming sulphuric acid with cooling, and pouring the mixture on to ice, crystallises from chlorobenzene as a greenish-yellow, crystalline powder, which decomposes without

previous melting. **3-Methyl- $\alpha\beta$ -anthraquinonylisooxazole**, prepared in a similar way, forms coarse, dark brown crystals, m. p. 210° . **5:6:7:8-Tetrachloro-2-methylanthraquinone** prepared in the usual manner from *o*-benzoyltetrachloro-*p*-methylbenzoic acid, forms a pale greenish-yellow powder, m. p. 192° . On nitration, it yields **5:6:7:8-tetrachloro-1-nitro-2-methylanthraquinone**, pale yellow crystals, m. p. 262° (decomp.). On treatment with fuming sulphuric acid at $5-10^\circ$, the nitro-compound is converted into **7:8:9:10-tetrachloro- $\alpha\beta$ -anthraquinonylisooxazole**, forming yellow, crystalline needles, m. p. 242° (decomp.).

According to the second patent (160433), the anthraquinonylisooxazoles are obtained in much greater purity if the reaction is conducted with exclusion of air, for example, in an atmosphere of carbon dioxide.
G. F. M.

NN'-Di(*p*-allyloxyphenyl)acetamidine. J. SCHULER (U.S. Pat. 1384637). NN'-Di(*p*-allyloxyphenyl)acetamidine, colourless crystals, m. p. $85-86^\circ$, readily soluble in alcohol and ether and insoluble in water, forming a hydrochloride, m. p. $152-153^\circ$, which dissolves easily in alcohol, is less soluble in water, and insoluble in ether, is adapted for use as a local anæsthetic in ophthalmological practice. It is prepared by condensing allyloxylaniline with *p*-allyloxyacetanilide in the presence of phosphorus pentoxide or similar condensing agent.
CHEMICAL ABSTRACTS.

Action of Iodine on NN'-Dialkyltetrahydro-4:4'-dipyridyls. BRUNO EMMERT and PAUL PARR (*Ber.*, 1921, **54**, [B], 3168-3176; cf. A., 1909, i, 602; 1917, i, 221; 1919, i, 455; 1920, i, 331).—The action of iodine on the blue solutions of dimethyl-, diethyl-, and dibenzyl-tetrahydrodipyridyls has been shown to lead to the production of the corresponding alkylpyridinium iodides and of amorphous, yellow substances containing iodine which have not been investigated more closely. The corresponding diisobutyl and diisomyl compounds are now shown to react in a similar manner, but, in addition, to give small amounts of the 4:4'-dipyridyldialkylidides
$$\begin{array}{c} \text{R} > \text{N} < \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} > \text{C} < \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} > \text{N} < \text{R} \\ \text{I} & & \text{I} \end{array}$$
 the mode of removal of the two hydrogen atoms in position "4" has not been elucidated fully.

Diisomyltetrahydrodipyridyl is converted by iodine in alcoholic solution into a yellow, amorphous product, *isomylpyridinium iodide* (*platinichloride*, $\text{C}_{20}\text{H}_{32}\text{N}_2\text{Cl}_2\text{Pt}$, pale yellow, rhombic leaflets) and 4:4'-dipyridyl diisomylidide; the latter substance is obtained readily from its components. It crystallises in long, thin, red prisms, m. p. $270-280^\circ$ (decomp.). When the cold aqueous solution of the salt is agitated with silver oxide, it gives a colourless solution of the *base*, which becomes blue when warmed, but again colourless when cooled or treated with air. The corresponding *bromide*, green plates, colourless *chloride*, and *platinichloride*, long, orange-yellow needles, m. p. $260-270^\circ$ (decomp.), are described.

4 : 4'-Dipyridyl diisobutiodide, red, rhombic leaflets, is prepared by the same methods as the isoamyl compound; the corresponding platinichloride has m. p. above 300° (decomp.).

The communication includes an exhaustive reply to the recent criticism of Weitz and Nelken (A., 1921, i, 804). H. W.

A Comparison of Three Isomeric Carbocyanines. WALTER THEODORE KARL BRAUNHOLTZ (T., 1922, 121, 169—173).

spiroPyrimidines. III. Condensation of cycloPropane-1 : 1-dicarboxylic Ester with Carbamides. ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1921, 43, 2097—2101; cf. A., 1921, i, 360, 740).—The yield of ethyl cyclopropane-1 : 1-dicarboxylate from ethylene bromide and ethyl malonate by the action of sodium ethoxide (cf. Perkin, T., 1885, 47, 808; 1887, 51, 849) was increased by modifying the conditions. The ester has b. p. 214—216°/748 mm. (corr.), the monoamide, m. p. 195°, and the diamide, m. p. 198°.

The ester condensed with carbamide, guanidine, and thiocarbamide to give stable amorphous compounds, which were apparently not spiropyrimidines, but polymerides. Hydrolysis of the polymeride from carbamide, followed by elimination of carbon dioxide, gave a crystalline acid, $C_8H_{12}O_4$, m. p. 152°. The probable course of the condensation of the ester and carbamide is that cyclopropane-1 : 5-spirobarbituric acid is first formed and this undergoes rearrangement to vinylbarbituric acid, which then polymerises, giving a cyclobutanedibarbituric acid. The latter acid on hydrolysis and loss of carbon dioxide should yield cyclobutane-1 : 2- or 1 : 3-diacetic acid, which could exist in *cis* and *trans* forms, but such acids are not yet known. W. G.

The Halogenated Indigotins. E. GRANDMOUGIN (*Compt. rend.*, 1921, 173, 1363—1365).—It is not possible to foretell with certainty the shade of colour of new indigotin derivatives. The marked influence of the positions 6 and 6' which prevent the tendency towards green of neighbouring groups, as shown in the case of octabromoindigotin (cf. this vol., i, 55), is further verified in the chloro-series, where octachloroindigotin is more violet than the 5 : 7 : 5' : 7'-tetrachloro-derivative. The absorption rays of certain di- and tetra-halogenated indigotins in solution in xylene or methyl benzoate are given. W. G.

Constitution of the Dipeptides of Aspartic Acid. C. RAVENNA (*Gazzetta*, 1921, 51, ii, 281—284).—Both the dipeptide of aspartic acid obtained by Fischer and Koenigs from diketopiperazinediacetic anhydride (A., 1907, i, 486) and that prepared by Ravenna and Bosinelli (A., 1920, i, 150, 151) from asparagine yield voluminous precipitates with lead acetate, but in the former case the precipitate is sparingly, and in the latter case readily, soluble in excess of the reagent. Further, the former dipeptide gives only a distinct blue coloration with copper sulphate and potassium hydroxide, whereas the latter gives the characteristic biuret reaction.

Diketopiperazinediacetic anhydride has been prepared from

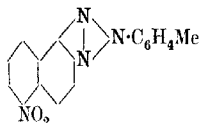
each of the two dipeptides and from ammonium hydrogen malate; the three preparations yield the β -dipeptide, unmixed with α -isomeride, when treated with barium hydroxide solution. It is possible also that the α -dipeptide may be obtainable directly from α -asparagine by boiling its aqueous solution.

These results confirm the constitutions previously ascribed to the two dipeptides (A., 1920, i, 600).

T. H. P.

6-Amino-2-p-tolyl- $\alpha\beta$ -naphthatriazole. GILBERT T. MORGAN and SYDNEY CHAZAN (*J. Soc. Chem. Ind.*, 1922, **41**, 11).—The investigation was undertaken with the object of securing a series of substituted α -naphthylamines capable of acting as middle components in the production of poly-azo-dyes. The difficulty with which they react with diazonium compounds, however, renders the 6-amino-2-aryl- $\alpha\beta$ -naphthatriazoles unsuitable for this purpose. On the other hand, these aminotriazoles yield stable, sparingly soluble diazo-derivatives which couple readily to form azo-compounds with the phenols and the more reactive aromatic bases.

5-Nitro- β -naphthylamine, m. p. 140–142°, is prepared by the action of concentrated sulphuric acid below –5° on β -naphthylamine nitrate and is converted by a diazotised solution of *p*-toluidine into *p*-toluene-1-azo-5-nitro- β -naphthylamine, red, nodular crystals, m. p. 197–199° after softening at 190°. The latter substance is oxidised by chromic acid in acetic acid solution to 6-nitro-2-p-tolyl-



$\alpha\beta$ -naphthatriazole (annexed formula), yellow, flaky crystals, m. p. 207–208°.

6-Amino-2-p-tolyl- $\alpha\beta$ -naphthatriazole has m. p. 178–180°; the corresponding *hydrochloride*, m. p. 263–267° (decomp.) after softening at 240°, and *acetyl* derivative, light brown needles, m. p. 305–307°, are described. A diazotised solution of the aminotriazole couples with β -naphthol in alkaline solution, giving *p*-tolyl- $\alpha\beta$ -naphthatriazoleazo- β -naphthol, m. p. (indefinite) 250–260°. With *p*-nitrobenzenediazonium chloride, the aminotriazole gives 7-p-nitrobenzeneazo-6-amino-2-p-tolyl- $\alpha\beta$ -naphthatriazole, a sparingly soluble, brownish-red compound, m. p. 195–197° (decomp.), which is oxidised by chromium trioxide in hot glacial acetic acid to a brown, *bistriazole* derivative, m. p. 220–240° (decomp.) after softening at 210°.

H. W.

The Velocity of Reaction of Diazotisation in its Bearing on the Problem of Substitution in the Benzene Ring. II. The Character of the Diazonium Group. H. A. J. SCHOUTSEN (*Rec. trav. chim.*, 1921, **40**, 763–774; cf. Martinsen, A., 1907, ii, 609).—As a result of failure in attempts to nitrate benzene-diazonium sulphate, it is inferred that the diazonium group is very strongly negative, more so than the nitro-group, and its directing influence on entering groups is towards the meta-position. Para-substituted-amino-diazonium compounds have also been dealt with and similar results obtained, except in the case of the *p*-amino-phenoldiazonium compound. The author puts forward an

alternative explanation to that of Cain (T., 1907, **91**, 1049) with regard to certain phenomena in diazo-compounds. H. J. E.

Method for the Separation of Amino-acids from the Products of Hydrolysis of Proteins and Other Sources. HAROLD W. BUSTON and SAMUEL BARNETT SCHRYVER (*Biochem. J.*, 1921, **15**, 636—642).—A preliminary indication of a method whereby dicarboxylic amino-acids are precipitated by alcohol as barium salts, after saturating their aqueous solution with baryta. If then, without removing the alcohol, carbon dioxide is passed into the solution, other amino-acids are precipitated as barium carbamates (cf. Siegfried, A., 1906, i, 324). No individual amino-acid was isolated. G. B.

Estimation of the Monoamino-acids in the Hydrolytic Cleavage Products of Lactalbumin. D. BREESE JONES and CARL O. JOHNS (*J. Biol. Chem.*, 1921, **48**, 347—360).—The following results were obtained: Glycine 0.37%, alanine 2.41%, valine 3.30%, leucine 14.03%, proline 3.76%, phenylalanine 1.25%, aspartic acid 9.30%, glutamic acid 12.89%, hydroxyglutamic acid 10.00%, serine 1.76%, tyrosine 1.95%. E. S.

Swelling of Fibrin by Acids. R. SOMOGYI (*Biochem. Z.*, 1921, **120**, 103—105).—The swelling of fibrin by acids resembles the effect of acids on gelatin, the acids following the same order of activity. The biologically important acids, hydrochloric, lactic, and formic, produce pronounced swelling. H. K.

Alkaline Hydrolysis of Casein. MARY A. GRIGGS (*J. Ind. Eng. Chem.*, 1921, **13**, 1027—1028).—The maximum yield of amino-nitrogen (60% of the total nitrogen) is obtained when casein is heated at 150° under pressure for five hours with 10% sodium hydroxide solution. W. P. S.

The Influence of Electrolytes on the Solution and Precipitation of Casein and Gelatin. JACQUES LOEB and ROBERT F. LOEB (*J. Gen. Physiol.*, 1921, **4**, 187—211).—Two types of colloidal solution exist. The first type is easily precipitated by small quantities of neutral salts, the second requires much larger quantities. In the first type, the particles go into solution as the result of swelling in consequence of the Donnan equilibrium, and remain in solution as a result of the osmotic and electrical forces which the Donnan equilibrium necessitates. The second type is of the nature of true solution and there exist primarily only ions and molecules, although aggregates may be formed secondarily. Measurements of the rate of solution of casein chloride in varying concentrations of acids and neutral salts indicate that the process of solution is regulated by the Donnan equilibrium and that it is of the first type. Here the effect of small quantities of neutral salts as precipitants is to reduce the osmotic forces and also the electric charges, according to the theory of the Donnan equilibrium. Casein dissolves in sodium hydroxide solutions essentially like a crystalline substance, and the solution is of the second type. Solutions of gelatin are also of this type, although aggregates of

the dissolved particles tend to form on keeping (cf. A., 1921, i, 822). Experiments on the solubility and viscosity of gelatin solutions as influenced by neutral salts give evidence of the existence of these aggregates.

W. O. K.

Swelling of Gelatin in Aqueous Solutions of Organic Acids.

ALFRED KUHN (*Koll. Chem. Beihefte*, 1921, 14, 147—208).—The swelling of gelatin in aqueous solutions of various concentrations of a large number of organic acids has been determined by the so-called volume method at 20°, and from the results the increase in the swelling is ascertained in each case. A few experiments are described at 0°, 16°, and 22°, which were made to ascertain the influence of temperature on the swelling. The following acids were investigated: Formic, acetic, propionic, *n*-butyric, isobutyric, *n*-valeric, isovaleric, isooctioic, glycollic, lactic, chloroacetic, dichloroacetic, trichloroacetic, bromoacetic, cyanoacetic, oxalic, malonic, succinic, malic, *d*-tartaric, citric, maleic, fumaric, aminoacetic, benzoic, *m*-toluic, phenylacetic, salicylic, *m*-hydroxybenzoic, mandelic, benzenesulphonic, sulphanilic, cinnamic, phthalic, protocatechuic, gallic, tannic, and picric, also hydrochloric, sulphuric, and nitric acids, phenol, quinol, resorcinol, catechol, and naphthalene-1-sulphonic acid. It is shown that, with the exception of the sparingly soluble acids, all acids show a swelling maximum at a medium concentration. Swelling is the result of four simultaneous processes of which at least two operate in opposite directions. The first process is the actual swelling, *A* (hydration) and is the chief process at low concentrations; opposed to this are sol formation and hydrolysis, *B*; the fourth process is dehydration and coagulation. The swelling maximum is defined as that point at which the amount of swelling (*A*) with increasing concentration is exceeded by the sol formation (peptisation) and the decreasing hydrolysis (*B*). No relationship between the maximum swelling and the degree of dissociation of the acids could be found, but an approximate connexion between the concentrations at which the maximum occurs and the strength of the acid was found. With strong acids, the maximum swelling concentrations lie at lower concentrations and with weaker acids at higher concentrations, whilst with acids of medium strength the curve only shows a bend. The swelling maximum as the resultant of the hydration, sol formation, and hydrolysis shows no linear relationship, rather, especially in the case of acids of medium strength, does the sol formation appear to play the greater rôle. The actual swelling in the region of small concentrations is well represented by the equation $h = qC^n$, in which *h* is the swelling height, *C* the concentration of the acid, and *q* and *n* are constants. The principal part of the swelling can be quantitatively represented by the constants *q* and *n*. Neither *q* nor *n* has any connexion with the strength of the acid, and, further, the swelling maximum is not determined by either *q* or *n*. Hence it is shown that acids operate in the swelling of gelatin in the sense that at lower concentrations a specific increase in the power of binding water is

brought about. Whether thereby a chemical or adsorption compound is formed has not been settled. At higher concentrations, sol formation and hydrolysis commence and at the same time dehydration and precipitation, which are opposed to the actual swelling process.
J. F. S.

A New Function of the Tryptic Ferment (Anhydrase) and the Preparation of *d*-Tyrosine-anhydride and *d*-Tryptophan-anhydride from the Products of Tryptic Digestion. SIGMUND FRÄNKEL and EMIL FELDSEBERG (*Biochem. Z.*, 1921, **120**, 218—229).—Casein, when digested with trypsin until the bromine test for tryptophan is negative, yields a dextrorotatory tyrosine-anhydride and a dextrorotatory tryptophan-anhydride. The amino-groups are free, but the carboxyl groups are combined as in acetic anhydride. *d*-Tyrosine-anhydride has m. p. 273° and $[\alpha]_D^{20} + 37.59^\circ$ in alkaline solution, $[\alpha]_D^{20} + 93.87^\circ$ in acid solution. *d*-Tryptophan-anhydride decomposes at 230—245° and has $[\alpha]_D^{20} + 20.59^\circ$ in water.
H. K.

The Activity of Adsorbed Invertase. J. M. NELSON and DAVID I. HITCHCOCK (*J. Amer. Chem. Soc.*, 1921, **43**, 1956—1961).—The result obtained by Nelson and Griffin that a given quantity of invertase exhibited the same activity when adsorbed on a solid in the bottom of the reaction vessel as when uniformly distributed throughout the solution (cf. A., 1916, i, 516) is not general, but represents only a special case. It is now shown that, other conditions being equal and the velocity of hydrolysis relatively large, the amount of sucrose hydrolysed in a given time is less in the presence of an adsorbent. The decrease in rate is apparently due largely to the uneven distribution of the invertase in the reaction mixture, and the extent of the retardation may be considerably diminished by stirring the mixture and thus preventing the settling of the adsorbent. Results comparable with those of Nelson and Griffin (*loc. cit.*), are obtained only when the velocity of hydrolysis is relatively small, and it is suggested that, under these conditions, the rate of diffusion of the sucrose to, and of the invert-sugar from, the enzyme combined with the adsorbent is probably greater than the rate of hydrolysis of the sucrose.
W. G.

The Distinctive Properties of Amylases from Different Sources. JEAN EFFRONT (*Compt. rend.*, 1922, **174**, 18—21).—Amylases from different sources may be distinguished from one another by the ratio of their liquefying power to their saccharifying power, by the intensity of their saccharifying power, by their optimum temperatures, by their resistance to temperatures of 70—100°, and by their action at 20°. Some amylases in juices or extracts when heated at 60° and filtered recover after filtration their activity lost during heating, whilst other amylases lose their activity altogether.
W. G.

A Study of the Catalase of Flour. T. MERL and J. DAIMER (*Z. Unters. Nahr. Genussm.*, 1921, **42**, 273—290).—A catalase was prepared from the wheat embryo having five times the activity

of ordinary flour. The optimum hydrogen-ion concentration for the catalase corresponds with $p_H=6.2-7.1$; and the optimum temperature is $30-40^\circ$ with a temperature coefficient of approximately 1.5. The catalase is relatively resistant to dry heat, but extremely sensitive to moist heat. It is less affected by toluene than by alcohol, benzene, or hydrocyanic acid. [Cf. *J. Soc. Chem. Ind.*, 1922, 114 A.] A. G. P.

Decomposition of Amygdalin from the Point of View of Conjugated Fermentation. J. GIAJA (*J. Chim. Physique*, 1921, 19, 77-99).—The decomposition of amygdalin by emulsin from *Helix pomatia* and by emulsin from almonds at $37-40^\circ$ takes place in two stages with intermediate products which are different in the two cases. The fermentation decomposition of amygdalin is not a simple process; the decomposition is a conjugated or coupled fermentation made up at least of two reactions, a primary and a secondary fermentation. The decomposition of amygdalin by the above-named emulsins is probably an unique case in which it is possible to follow exactly the progress of both the primary and secondary fermentations. The two actions constituting the couple are within certain limits independent of one another, for it is shown that changes in the concentration of amygdalin, ferment, dextrose, hydrocyanic acid, and benzaldehyde, as well as ultra-violet light affect the two reactions differently. The ratio in which the dextrose and hydrocyanic acid appear in the course of the reaction with emulsin from *Helix pomatia* varies with the speed of the reaction, that is to say, with the concentration of the ferment. The more rapid the reaction the more nearly does the ratio approach that in which the dextrose and hydrocyanic acid exist in amygdalin. The influence of the initial concentration of amygdalin on the secondary reaction with both ferments is that the secondary reaction proceeds more rapidly when the initial concentration is small. The influence of an addition of dextrose is different in the case of the two ferments, but in both cases it only affects the reaction which produces dextrose. The addition of benzaldehyde and hydrocyanic acid retards the reaction in which these substances respectively are produced. Thus whilst dextrose and hydrocyanic acid affect the fermentation reaction itself, benzaldehyde acts on the ferment and destroys it. Ultra-violet rays affect the reaction with emulsin from *Helix pomatia* in the sense that the formation of dextrose is more rapid than that of hydrocyanic acid. If the reaction with emulsin from *Helix pomatia* is stopped before completion by heating, and emulsin from almonds is added, it is found that the reaction does not go so far as either ferment alone would have taken it. Thus emulsin from almonds cannot complete the reaction started by emulsin from *Helix pomatia*, but emulsin from *Helix pomatia* can complete the reaction started by emulsin from almonds. J. F. S.

Urease. STURE LÖVGREN (*Biochem. Z.*, 1921, 119, 215-293).—This paper contains a valuable bibliography of 212 papers, and is illustrated throughout with quotations from original papers.

The author has carried out experiments covering a wide range of properties of urease, but the main portion deals with an attempt to find the time equation which covers the reaction adequately. Van Slyke and Cullen's equation was found not to hold, but a simple, apparently empirical, modification of the unimolecular equation gave excellent results provided that at each concentration of urea the solution was kept at the particular optimum P_{11} .

H. K.

Additive Reactions of Phosphorus Haloids. IV. The Action of the Trichloride on Saturated Aldehydes and Ketones.

J. B. CONANT, A. D. MACDONALD, and A. McB. KINNEY (*J. Amer. Chem. Soc.*, 1921, 43, 1928—1935).—It has previously been shown that benzaldehyde reacts with phosphorus trichloride in acetic acid to give good yields of an α -hydroxyphosphinic acid (cf. A., 1921, i, 69). It is now shown that the reaction can be extended to other aldehydes and ketones, although with ketones it is of somewhat limited scope and in certain cases it was found desirable to replace the acetic acid by benzoic acid as the medium and work at 150° instead of below 30°.

The hydroxyphosphinic acids were difficult to isolate in the crystalline state and in some cases could only be obtained as their lead salts. With acetophenone and acetone, an unsaturated phosphinic acid was also, in each case, produced, but only isolated from acetophenone. The following new compounds are described: α -Phenylvinylphosphinic acid, $\text{CH}_2=\text{CPh}\cdot\text{PO}_3\text{H}_2$, m. p. 112°; α -hydroxy- α -methylpropylphosphinic acid isolated as its lead salt; α -hydroxy- α -ethylbutylphosphinic acid as its lead salt; α -hydroxy- α - β -trimethylpropylphosphinic acid as its lead salt; α -hydroxy- β -phenyl- α -benzylethylphosphinic acid, m. p. 181—182°; α -hydroxy- α -diphenylpropylphosphinic acid, m. p. 165—168°; α -hydroxy- γ -phenyl- α -(β -phenylethyl)propylphosphinic acid, m. p. 173—174°; α -hydroxydiphenylmethylphosphinic acid, m. p. 171—172°. Additive products could not be obtained with benzil or anthraquinone.

W. G.

The Relation between the Mode of Synthesis and Toxicity of Arsphenamine [Salvarsan] and Related Compounds.

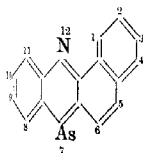
WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1921, 43, 2202—2210).—The variation in toxicity of different samples of salvarsan prepared by reduction of 3-nitro-4-hydroxyphenylarsinic acid by hyposulphite is due to variations in the experimental conditions during the reduction of the nitro-group. To obtain a sample of low toxicity a cold solution of the nitro-compound should be added to a cold solution of magnesium chloride and sodium hyposulphite with vigorous stirring. The mixture is then rapidly heated at 40° after the addition of vegetable charcoal and filtered, the filtrate being rapidly heated at 55°. If the solutions are mixed warm with slow stirring and the mixture only slowly raised to 55° a salvarsan of high toxicity is obtained. For the consistent production of salvarsan of the lowest toxicity it is advisable to use pure 3-amino-4-hydroxyphenylarsinic acid as the starting material, in

which case there is no need to adhere strictly to the conditions at the beginning. This variation in toxicity is apparently general to the aminoarylseno-compounds. It has been found with 3-amino-4:4'-dihydroxyarsenobenzene hydrochloride, 3:5:3'-tri-amino-4:4'-dihydroxyarsenobenzene trihydrochloride, and 3:5:3':5'-tetra-amino-4:4'-dihydroxyarsenobenzene tetrahydrochloride. The variation in toxicity is due to the formation of by-products, during the reduction of the nitro-group, which unite with the amino-acid in the subsequent reduction of the arsenic acid group, giving unsymmetrical arseno-compounds. W. G.

Arsenated Benzophenone and its Derivatives. W. LEE LEWIS and H. C. CHEETHAM (*J. Amer. Chem. Soc.*, 1921, **43**, 2117—2121).—Dichloro-*p*-arsinobenzoyl chloride condenses quite readily with aromatic hydrocarbons and phenyl ethers in the presence of anhydrous aluminium chloride, using carbon disulphide as a solvent. Thus with benzene, after warming the product with aqueous sodium hydroxide, *benzophenone-p-arsenious oxide*, $\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}$, was obtained, which on boiling with water gave *benzophenone-p-arsenious acid*, $\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{As}(\text{OH})_2$, and on oxidation with hydrogen peroxide yielded *benzophenone-p-arsinic acid*, $\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$, giving an oxime. On nitration, the arsenic acid gave *nitrobenzophenone-p-arsinic acid*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$. Other compounds, similarly prepared, are 4-methylbenzophenone-4'-arsenious oxide; 4-methylbenzophenone-4'-arsinic acid; 4-methoxybenzophenone-4'-arsinic acid; 4-ethoxybenzophenone-4'-arsinic acid, and 4-phenoxybenzophenone-4'-arsinic acid. *p*-Carboxyphenylarsinic acid is best obtained for these preparations from *p*-aminobenzoic acid by Bart's method (Ger. Pat. 250264 and 254345) and subsequently converted into dichloro-*p*-arsinobenzoyl chloride by Poulenc's method (French Pat. 441215). W. G.

4-Carboxy-2-phenylquinoline-6-arsinic acid. J. R. JOHNSON and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1921, **43**, 2255—2257).—When pyruvic acid is added to a boiling solution of arsanilic acid and benzaldehyde in absolute alcohol and the mixture boiled for four hours 4-carboxy-2-phenylquinoline-6-arsinic acid, m. p. 186—187° (corr.) (decomp.), is obtained. It gives a neutral disodium and a slightly alkaline trisodium salt, a green copper salt, yellow silver, lead, mercurous, mercuric, and cadmium salts, and reddish-brown cobalt and ferric salts. W. G.

7-Chloro-7:12-dihydro- γ -benzophenarsazine and some of its Derivatives. W. LEE LEWIS and C. S. HAMILTON (*J. Amer. Chem. Soc.*, 1921, **43**, 2218—2223).—The annexed constitution is considered as probably that of γ -benzophenarsazine.



Phenyl- α -naphthylamine readily reacts with arsenic trichloride to give 7-chloro-7:12-dihydro- γ -benzophenarsazine, m. p. 219°, which is physiologically much less irritant than the corresponding diphenylchloroarsine. It readily reacts with sodium alkylloxides or arylloxides

to give stable alkyloxy- or aryloxy-derivatives of the type $\text{NH} \langle \text{C}_6\text{H}_5 \rangle \text{As} \cdot \text{OR}$. The following are described: 7-Methoxy-7:12-dihydro- γ -benzophenarsazine, m. p. 209°; 7-ethoxy-7:12-dihydro- γ -benzophenarsazine, m. p. 165°; 7-n-propoxy-7:12-dihydro- γ -benzophenarsazine, m. p. 152°; 7-n-butoxy-7:12-dihydro- γ -benzophenarsazine; 7-phenoxy-7:12-dihydro- γ -benzophenarsazine, m. p. 179°; 7-benzylaxy-7:12-dihydro- γ -benzophenarsazine, m. p. 154°. When oxidised in acetic acid solution by hydrogen peroxide, 7-chloro-7:12-dihydro- γ -benzophenarsazine gives γ -benzophenarsazinic acid, $\text{NH} \langle \text{C}_6\text{H}_5 \rangle \text{As}(\text{OH})_3$, giving a sodium salt. Freshly precipitated silver oxide reacts in ammoniacal solution with 7-chloro-7:12-dihydro- γ -benzophenarsazine to give 7:12-dihydro- γ -benzophenarsazine oxide, $(\text{NH} \langle \text{C}_6\text{H}_5 \rangle \text{As})_2\text{O}$. The corresponding sulphide, 7:12-dihydro- γ -benzophenarsazine sulphide, m. p. 204–205°, was obtained by bubbling hydrogen sulphide through an alcoholic solution of the chloro-compound. When boiled with an excess of hydrobromic acid 7-phenoxy-7:12-dihydro- γ -benzophenarsazine gave 7-bromo-7:12-dihydro- γ -benzophenarsazine, m. p. 227°. 7-Iodo-7:12-dihydro- γ -benzophenarsazine, m. p. 205°, was similarly prepared. Diphenylhydrazine when warmed with arsenic trichloride gives 6-chlorophenarsazine. W. G.

Organo-derivatives of Bismuth. V. The Stability of Halogen, Cyano-, and Thiocyno-derivatives of Tertiary Aromatic Bismuthines. FREDERICK CHALLENGER and JOHN FREDERICK WILKINSON (T., 1922, 121, 91–104).

Organo-derivatives of Bismuth. VI. The Preparation and Properties of Tertiary Aromatic Bismuthines and their Interaction with Organic and Inorganic Halogen Compounds. FREDERICK CHALLENGER and LESLIE RANDAL RIDGWAY (T., 1922, 121, 104–120).

Aromatic Mercuri-organic Derivatives. The Hofmann Rearrangement and the Nature of Valencies of Mercury in Mercuri-organic Derivatives. MORRIS S. KHARASCH (J. Amer. Chem. Soc., 1921, 43, 1888–1894).—Mercury diphenyl reacts with various acyl halogen amides in dry benzene, giving phenyl mercury haloid and the alkylcarbimide, the mercury diphenyl thus playing the same part as sodium hydroxide in aqueous solution or sodium ethoxide in absolute alcohol, and the amide undergoes the Hofmann rearrangement. Thus with *N*-bromoacetamide, the products are mercury phenyl bromide and methylcarbimide, similar changes occurring with *N*-bromobenzamide and with *m*-nitro-*N*-bromobenzamide. On the other hand, *N*-substituted alkyl or aryl bromo- and chloro-acetamides do not react with mercury diphenyl any more than they undergo rearrangement with sodium hydroxide or ethoxide. The mercury diphenyl thus acts as a base in benzene solution, being a base of the benzene system in the same way as sodamide is of the ammonium system.

The author does not consider that the electronic structure for mercury diaryl compounds proposed by Jones and Werner (A., 1918, i, 483) has any sound theoretical or experimental basis, and proposes as an alternative structure, $\bar{R}-\overset{++}{\text{Hg}}-\bar{R}$. The formation of metallic mercury and benzyl acetate when mercury diphenyl is hydrolysed by glacial acetic acid at 200° (Jones and Werner, *loc. cit.*) is due to intramolecular oxidation and reduction. W. G.

Mercuri-organic Derivatives. The Mercurisation of Aromatic Amines and its Relation to the Theory of Substitution. MORRIS S. KHARASCH and ISADORE M. JACOBSON (J. Amer. Chem. Soc., 1921, 43, 1894—1903).—Schoeller, Schrauth, and Liese (cf. A., 1920, i, 120), in their theory of mercurisation, assume that the entrance of a group into the nucleus of an aromatic amine is always preceded by substitution on the amino-nitrogen. This theory does not explain, however, the mechanism of substitution in the case of tertiary amines, such as dimethylaniline, which contain no replaceable hydrogen. The authors propound the theory that of the aromatic amines only those which are capable of forming salts will mercurise and that mercurisation is always preceded by addition of a mercuric salt to the amino-nitrogen, with subsequent rearrangement of the mercury to the ortho- or para-position. This theory also applies equally well, without further postulates, to the introduction of other groups into the benzene nucleus in the case of aromatic amines. Where such salt formation is not possible, as in the quaternary ammonium salts, substitution must take place in the meta-position or, as in such special cases as that of mercurisation, it is not accomplished at all.

Thus *p*-nitrodimethylaniline, which is an extremely weak base and does not form salts, would not mercurise, whereas *p*-nitromethylaniline mercurised without difficulty. In further support of the theory, unpublished work is mentioned in which the intermediate additive compound from *m*-nitroaniline and mercuric acetate was isolated.

The following compounds are described. *o*-Nitro-*p*-acetoxymercuridimethylaniline, m. p. 160°; *o*-nitro-*p*-chloromercuridimethylaniline, m. p. 185° (decomp.); *m*-nitro-*p*-acetoxymercuridimethylaniline, m. p. 140°; *m*-nitro-*p*-chloromercurimethylaniline, m. p. 220° (decomp.); *p*-nitro-*o*-acetoxymercurimethylaniline, m. p. 197° (decomp.); *p*-nitro-*o*-chloromercurimethylaniline, m. p. 215° (decomp.); *p*-nitro-*o*-acetoxymercuriethylaniline, m. p. 183°; *p*-nitro-*o*-chloromercuriethylaniline, m. p. 218° (decomp.).

For purposes of characterisation, 2-bromo-4-nitroethylaniline, m. p. 65–66°; and 2:6-dibromo-4-nitroethylaniline, m. p. 75–76°, were prepared by brominating *p*-nitroethylaniline in acetic acid solution, using the requisite proportions of bromine. W. G.

An Indirect Method of Preparation of Organic Mercuric Derivatives and a Method of Linking Carbon to Carbon. MORRIS S. KHARASCH (J. Amer. Chem. Soc., 1921, 43, 2238—2243).—When mercuric salts of certain carboxylic acids are heated, carbon

dioxide is split off and the mercury takes the place originally occupied by the carboxyl group. Thus *mercuric 2:4-dinitrophenylacetate* when heated at 180° gives *mercury 2:4:2':4':tetranitrodibenzyl*, $C_6H_3(NO_2)_2 \cdot CH_2 \cdot Hg \cdot CH_2 \cdot C_6H_3(NO_2)_2$, m. p. 235° ; and *mercuric 2:4:6-trinitrobenzoate* gives *mercury 2:4:6:2':4':6':hexanitrodiphenyl*, m. p. 272° . The latter compound when heated in alcohol with mercuric chloride gives *2:4:6-trinitrophenyl mercurichloride*, $C_6H_3(NO_2)_3 \cdot HgCl$, m. p. 202° , which, when treated in aqueous suspension with iodine in potassium iodide solution gives *2:4:6-trinitroiodobenzene* and a compound which is probably *2:4:6:2':4':6'-hexanitrodiphenyl*. It is thought that by heating these mercury compounds in the dry state or in some solvent the mercury would oxidise one of the carbon atoms and thereby link the two carbon atoms together. This was observed in the case of *2:4:2':4'-tetranitromercurydibenzyl*, tetranitrodibenzyl being obtained.

This work is being extended to mercury salts of various types of carboxylic acids. W. G.

Physiological Chemistry.

The Excretion of Acetone from the Lungs. A. P. BRIGGS and PHILIP A. SHAFFER (*J. Biol. Chem.*, 1921, **48**, 413—428).—Experiments on human diabetics, normal fasting subjects, and dogs after injection of large doses of acetone, show (1) that acetone is distributed between blood and alveolar air in approximately the same ratio as between water and air, (2) that the concentration of acetone in urine is approximately the same as in blood. These results confirm Widmark's conclusion (*Biochem. J.*, 1920, **14**, 379) that acetone is excreted from the lungs and kidneys by the physical process of diffusion. E. S.

Physical Chemistry of Cell Respiration. OTTO WARBURG (*Biochem. Z.*, 1921, **119**, 134—166).—The adsorption and oxidation of cystine by blood charcoal was investigated in the presence of various narcotics. There is an inhibition of both properties due to a displacement of the amino-acid and of oxygen from the charcoal surface by the narcotic. Hydrocyanic acid also inhibits adsorption and oxidation, but the same explanation does not hold good. A comparison was made of blood charcoal and charcoal prepared from benzoic acid. In composition and qualities of adsorption they differ markedly. From analogy with the charcoal experiments, cell respiration is considered to be essentially associated with the solid constituents of the cells. H. K.

Blood-gas Analysis. IX. Narcosis and Charge on the Colloids. KLOTHILDE MEIER and W. KRÖNIG (*Biochem. Z.*, 1921, **119**, 1—15).—By following the curve of combination of carbon dioxide with corpuscles as used in previous papers (A., 1920, i, 200), the authors show that addition of narcotics favours the neutralisation of the charge on the surface colloids of the erythrocytes. Corpuscles suspended in saline solution are discharged at P_H 6.87, but at the optimum concentration in the saline of methylurethane, ethylurethane, and ethyl alcohol the discharge takes place at P_H 6.95, 6.90, and 6.85 respectively. H. K.

The Dextrose Concentration in the Arterial Blood and in the Venous Blood from the Muscles. V. HENRIQUES and R. EGE (*Biochem. Z.*, 1921, **119**, 121—133).—No great difference of dextrose content between arterial and venous blood is to be expected. The process is complicated by a reservoir of carbohydrate in the muscles. Under special conditions, a difference can be observed. In a condition of hyperglycæmia, there is a large disappearance of dextrose during passage through the muscles, and when the dextrose concentration in the blood has again fallen the venous blood may contain more than the arterial. H. K.

The Ammonia Content of the Blood and its Bearing on the Mechanism of Acid Neutralisation in the Animal Organism. THOMAS P. NASH, jun., and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1921, **48**, 463—488).—The work of previous investigators on the ammonia content of the blood is discussed, and an improved technique for its estimation is described. The ammonia is removed from the blood by aeration, collected in acidified water, and estimated by means of Nessler's reagent.

By means of this method, the authors find concentrations of ammonia nitrogen varying from 0.03 to 0.20 mg. per 100 c.c. The concentration of ammonia in the blood is unaffected by the administration of phloridzin, the removal of the kidneys, and the injection of acid or alkali; the concentration in the renal venous blood is about twice as great as that in the systemic arterial blood.

From these results, the authors conclude that the kidney is the seat of formation of ammonia, and on this basis they offer an explanation of the different types of acidosis met with in various clinical conditions. C. R. H.

Inorganic Blood Phosphate. EDWIN P. LEHMAN (*J. Biol. Chem.*, 1921, **48**, 293—303).—A number of estimations of inorganic phosphate in the whole blood of normal rabbits by the method of Bell and Doisy (A., 1920, ii, 769) show that this constituent is practically constant and amounts to between 4 and 6 mg. per 100 c.c. When the concentration of phosphate is increased by the injection of large amounts of di-sodium hydrogen phosphate (sufficient in some cases to cause tetany) a normal concentration is reached again in four hours. C. R. H.

The Blood Calcium Content in Normal Children and in Tetany. I. B. DE VRIES ROBLES (*Nederl. Tijdschr. Geneesk.*, 1919, **63**, [j], 1663).—Despite statements to the contrary, there appears to be no abnormality in the content of calcium of the blood of children with tetany.

CHEMICAL ABSTRACTS.

The Blood-sugar in Narcosis and Diseases of the Nervous System. H. CHANTRAINE (*Zentr. inn. Med.*, 1920, **41**, 521—529).—During ether narcosis, the blood-sugar is increased, the increase ranging from 30 to 50%. During narcosis with ethyl chloride, in patients with nervous diseases, and in rabbits with experimentally produced concussion of the brain, the proportion of blood-sugar remains normal.

CHEMICAL ABSTRACTS.

Acetone Substances in the Blood in Diabetes. R. FITZ (*Trans. Assoc. Amer. Physicians*, 1917, **32**, 154—158).—Simultaneous estimation of the total acetone substances in the blood plasma and the degree of acidosis revealed no quantitative relationship between increased concentration of acetone and lowering of blood bicarbonate, although in general the proportion of the acetone rose as that of the bicarbonate fell. The total acetone was increased by large amounts of fat, the maximum occurring several hours after ingestion and after visible lipæmia had disappeared. Small amounts of fat depressed blood acetone. Fasting and pure carbohydrate diet diminished a high acetone value. Sodium hydrogen carbonate increased the output of acetone, but its effect on blood acetone was uncertain. In three fatal cases of coma, a rapid pre-mortar rise of blood acetone occurred; in one case this was independent of acidosis.

CHEMICAL ABSTRACTS.

Effect of Subcutaneous Injections of Solutions of Potassium Cyanide on the Catalase Content of the Blood. WILLIAM H. WELKER and J. L. BOLLMAN (*J. Biol. Chem.*, 1921, **48**, 445—451).—The subcutaneous injection in dogs of lethal doses of potassium cyanide has little, if any, effect on the catalase content of the blood.

E. S.

A Direct Demonstration of the Impermeability of the Corpuscles of Man and of the Rabbit for Dextrose. S. VAN CREVELD and R. BRINKMAN (*Biochem. Z.*, 1921, **119**, 65—72).—Corpuscles obtained by the jugular method from rabbits or by the paraffined tube method from man, are always free from dextrose. Faulty technique is the basis of the discrepant results of other workers.

H. K.

Colloidal Structure of Red Blood Corpuscles and Hæmolysis. III. Ultramicroscopic Investigation of Lipoids. KENZO HATTORI (*Biochem. Z.*, 1921, **119**, 45—64).—The colloidal balance of an optically homogeneous cholesterol-lecithin mixture is altered by water owing to swelling of the lecithin and separation of the cholesterol. By saline solution, however, the degree of swelling of lecithin is limited and there is no separation of cholesterol. Reagents which affect the colloidal balance are hæmolytic, but the parallelism is only approximate.

H. K.

The Combinations of Hæmoglobin with Oxygen and Carbon Monoxide, and the Effects of Acid and Carbon Dioxide.

ARCHIBALD VIVIAN HILL (*Biochem. J.*, 1921, **15**, 577—586).—A theoretical paper which suggests an explanation for the S-shaped dissociation curves of oxy-hæmoglobin and of carboxy-hæmoglobin and the identical effects of carbon dioxide on these curves. The chief assumptions made are (1) that hæmoglobin dissociates slightly into protein molecules and molecules containing iron, and (2) that in the presence of salts the osmotic pressure of the complex hæmoglobin and of the simpler protein is reduced to $1/n$ of its value, calculated on the basis of one atom of iron per molecule of hæmoglobin. This reduction is not necessarily due to aggregation of molecules, as was previously assumed (*J. Physiol.*, 1910, **40**, Proc. iv). It is shown that the effects of acid and of carbon dioxide on the dissociation curve of blood can be deduced from the hypothesis that the available alkali inside the corpuscle is competed for by oxy-hæmoglobin, reduced hæmoglobin, and the acid or carbon dioxide, the first being a far stronger acid than the second. The rectangular hyperbola relating carbon monoxide saturation to carbon monoxide pressure, or oxygen saturation to oxygen pressure, in blood or hæmoglobin fully saturated with a mixture of these gases, is also explained by the theory, as are various other points.

G. B.

Acceleration of Blood-clotting by Euphylline. R. MEISSNER (*Biochem. Z.*, 1921, **120**, 197—202).—Euphylline (an additive product of theophylline and ethylenediamine) can accelerate blood-clotting even up to 50%. The components have individually a weak action.

H. K.

The Basal Metabolism and the Specific Dynamic Action of Protein in Liver Disease.

JOSEPH C. AUB and JAMES H. MEANS (*Arch. Intern. Med.*, 1921, **28**, 173—191).—The basal metabolism in twelve cases of liver disease (gallstones, cirrhosis, carcinoma, acute catarrhal jaundice) was essentially within normal limits. The liver is, therefore, either not an important regulator of the metabolic rate, or it is adequate for this purpose even when severely diseased. The rate of absorption and utilisation of protein in large quantities was usually normal, even in severe cirrhosis. In two cases of cirrhosis and one of gallstones, the utilisation of the protein was delayed or absent. Marked portal obstruction caused no delay in the appearance of the specific dynamic action of protein. The cases of cirrhosis showed, on the whole, the highest metabolic response to protein katabolism. The conclusion seems justified that either the liver is not the main site of the specific dynamic action of protein, or that it can adequately perform that function even in disease. The specific dynamic action of protein results from an increased combustion of protein and carbohydrate, rather than of fat. The observations of Du Bois (*ibid.*, 1916, **17**, 115), that in exophthalmic goitre a normal increase in heat production, due to protein, is superimposed on the high basal rate, is confirmed.

CHEMICAL ABSTRACTS.

The Influence of Food Ingestion on Endogenous Purine Metabolism. I and II. WILLIAM C. ROSE (*J. Biol. Chem.*, 1921, **48**, 563—573 and 575—590).—The uric acid output remains constant under constant dietetic conditions, but is influenced by the quantity and nature of the food. In particular, it is increased by the amino-acids. The precursors of the purines are probably arginine and histidine; in the absence of these precursors, variations in the purine output may be brought about by the re-utilisation for anabolic purposes of purines produced in catabolism.

C. R. H.

Mechanism of Reduction of Nitrates and Nitrites in Processes of Assimilation. OSKAR BAUDISCH (*J. Biol. Chem.*, 1921, **48**, 489—502).—A summary of the author's previously published work on the subject.

E. S.

Quantitative Estimation of the Fat-soluble Factor. SYLVES-TER SOLOMON ZILVA and MASATARO MIURA (*Biochem. J.*, 1921, **15**, 654—659).—Rats are used which have been kept 3—4 weeks on the basal diet without growing; their weight should not exceed 70 grams. The minimum dose of the active substance is then determined which just induces a definite growth. For instance, 1.7 mg. of the most active cod liver oil per day did this, and 1.4 mg. did not. The minimum doses of various samples of cod liver oil varied from 1.7—5 mg., of butter from 200—400 mg.

G. B.

Pharmacological and Chemical Study of the Roes of the Barbel and Pike. FRANCIS H. McRUDDEN (*Arch. exp. Path. Pharm.*, 1921, **91**, 46—80).—Fish poisoning produced by consumption of the barbel or pike is due to a toxic substance contained mainly, if not exclusively, in the hard roes of these fishes. For the investigation of its properties the globulin and albumin were extracted from the roes by salt solution. On separation of these by the usual methods, the toxic action was found to be confined to the albumin fraction. Injected intravenously into rabbits, it produced paralysis of the central nervous system, death finally resulting from paralysis of respiration. The effects produced by extracts of the roes of either fish were similar, but more marked in the case of the pike. The toxicity is destroyed by heat. A comparison is made of the globulins (ichthulins) from eggs of various fish and the difference between their chemical properties and those of vitellin from birds' eggs emphasised.

E. S.

Zinc and Copper Content of the Human Brain. MEYER BODANSKY (*J. Biol. Chem.*, 1921, **48**, 361—364).—Analyses of one fetal and four adult brains indicate that zinc and copper are normal constituents of the human brain.

E. S.

Acetone in Cerebrospinal Fluid. J. KOOPMAN (*Nederl. Tijdschr. Geneesk.*, 1920, **64**, 1346—1350).—Acetone is present in the cerebrospinal fluid during diabetic coma, diabetic acidosis, and adrenal apoplexy; in the first two cases it is accompanied by acetoacetic acid.

CHEMICAL ABSTRACTS.

The Spacial Separation of Glycogen and Diastase in the Liver Cells. E. J. LESSER (*Biochem. Z.*, 1921, **119**, 108—120).—Perfusion of a frog's liver in the months August to January with hypertonic salt solutions leads to a fourfold excretion of dextrose over that produced by isotonic salt solutions. The dextrose production rises to a maximum after four hours. In the spring and summer months, there is no great difference between the effect of isotonic and hypertonic salines. This effect is independent of the ions of the salts used, and is only slightly affected by the hydrogen-ion concentration. The action appears to be purely osmotic.

H. K.

Sea-wolf Liver Oil. THOR LEXOW (*Chem. Umschau*, 1921, **28**, 213—214).—The livers were obtained from both male and female of the species *Anarrhichas lupus*, L.; the oil, extracted separately, was of a clear golden brown colour and had a curious odour unlike that of other liver oils. The oils from the male and female livers gave respectively the following characters: d_{4}^{25} 0.9162, 0.9179; n_D^{25} 1.4733, 1.4702; acid number 13.11, 14.37; saponification number 182.8, 185.2; iodine number (Wijs) 131.2, 118.1; unsaponifiable matter 5.23, 3.86; fatty acids 92.4%, 92.2%; m. p. of fatty acids 24.5°, 24.7°; mean molecular weight of the fatty acids 276.8, 279.9.

The oil is used in Russia mixed with coal-fish liver oil in tanning and can easily be distinguished from the sea-wolf liver oil by its low iodine number and high content of unsaponifiable matter.

H. C. R.

Variations in the Amylolytic Activity of the Pancreas and Liver in Avian Polyneuritis. R. TIGER and H. SIMONNER (*Bull. Soc. Chim. Biol.*, 1921, **3**, 580—582).—The amylolytic activity of the pancreas in pigeons with polyneuritis is slightly less than in normal birds. Experiments with the liver did not yield concordant results.

E. S.

The Function of the Pancreas. LEO ADLER (*Arch. exp. Path. Pharm.*, 1921, **91**, 110—124).—The author has previously shown that hibernating hedgehogs are roused and the body temperature brought to summer level by subcutaneous injection of extracts of thyroid or thymus, adrenaline, or certain amines derived from proteins. In the present paper, it is shown that a simultaneous injection of pancreas extract made from the pancreas of hibernating hedgehogs more or less completely suppresses the action of these substances. The suppression is less complete in the case of adrenaline than in the other cases.

E. S.

Heterogenetic Antigen and Hapten. XV. KARL LAND-STEINER (*Biochem. Z.*, 1921, **119**, 294—306).—The soluble heterogenetic antigens obtained from horse kidney by alcohol extraction are as active in vitro as the unchanged materials, but when injected into animals do not produce hæmolysin.

H. K.

The Enzymes of the Abdominal Adipose Tissue of the Common Turkey, *Meleagris gallinacea*. JOSEPH SAMUEL HEPBURN (*J. Amer. Chem. Soc.*, 1921, **43**, 1963—1965).—Using the method previously applied to chicken fat (cf. Pennington and Hepburn, A., 1912, ii, 273), but taking tributyrin as the substrate for lipase and ethyl butyrate for esterase, catalase, lipase, and esterase were always found in the adipose tissue. Simple reductase and oxydase acting on phenolphthalein were usually present. Tests for oxydases acting on α -naphthol and tricrosol, and for protease gave negative results. Aldehyde reductase and peroxydases were found in several of the samples. W. G.

The Selective Absorption of Potassium by Animal Cells.
II. The Cause of Potassium Selection as Indicated by the Absorption of Rubidium and Cæsium. PHILIP H. MITCHELL, J. WALTER WILSON, and RALPH E. STANTON (*J. gen. Physiol.*, 1921, **4**, 141—148).—Frog muscles, perfused with Ringer solution in which potassium has been replaced by cæsium (or rubidium) in equivalent amount, and stimulated electrically during the perfusion, absorb the cæsium (or rubidium) in such a way as to be retained during a subsequent perfusion with potassium-free Ringer solution. The substitution of cæsium (or rubidium) for potassium in the diet of rats leads to a replacement of potassium by that metal in the tissues. Rubidium and cæsium are toxic, and in the presence or absence of potassium cause death. The physiological peculiarities of these metals may be related to their electronic structure, and hence to their comparative migration velocities. W. O. K.

Physiological Significance of the Change in the Condition of Permeability in the Limiting Membrane of the Muscle Fibres. GUSTAV EMBDEN and ERICH ADLER (*Z. physiol. Chem.*, 1922, **118**, 1—49).—The permeability of the limiting sheath of the muscle fibres of the gastrocnemius of the frog was studied under different physiological conditions. The diffusion of phosphoric acid from the muscle into Ringer's solution was adopted as the method for the estimation of the permeability. S. S. Z.

Investigations on Potassium Paralysis. HANS VOGEL (*Z. physiol. Chem.*, 1922, **118**, 50—95).—The speed with which potassium paralysis intervenes in the gastrocnemius of the frog runs parallel with the permeability of the limiting membrane of the muscle fibres as determined by the diffusion of phosphoric acid out of the muscle (see preceding abstract). This, of course, depends on the physiological condition of the muscle. The onset of the potassium paralysis of the muscle can therefore be utilised as a standard for the permeability of the limiting membrane of the muscle fibres. The author utilises the above observation to explain the different conclusions drawn by himself and Overton in an earlier investigation. S. S. Z.

The Influence of Asphyxiation on the Permeability of the Limiting Membrane of the Muscle Fibres. MAX SIMON (*Z. physiol. Chem.*, 1922, **118**, 96—122).—Asphyxiation increases

the permeability of the limiting membrane of the muscle fibres in the gastrocnemius of the frog. This can be demonstrated by replacing oxygen by hydrogen. The change is reversible. The permeability was determined both by the diffusion of phosphoric acid and by the production of paralysis by the potassium ion (see preceding abstracts).

S. S. Z.

The Influence of the Chemical Composition and the Physico-chemical Structure on the Function of Frog Muscles.

HANS BEHRENDT (*Z. physiol. Chem.*, 1922, **118**, 123—167).—The lactacidogen content of the gastrocnemius and the adductor muscles of the frog is the same. The adductor muscles, however, contain sometimes more free phosphoric acid than the gastrocnemius. The "residual phosphoric acid" (restphosphorsäure) and the glycogen content is higher in the gastrocnemius than in the adductors. The physico-chemical properties of the two muscles as obtained by physiological methods are also compared.

S. S. Z.

Chemistry of the Formation and Ripening of Honey.

E. SARIN (*Biochem. Z.*, 1921, **120**, 250—258).—Bees were fed with sucrose syrup, the honey collected and re-fed to the bees. This process was repeated three times. Examination of the honey at each stage indicated that invertase and diastase are specific products of the bees, but catalase, which only occurs in natural honey, is of plant origin.

H. K.

Influence of Organic Acids on the Formation and Ripening of Sugar-honey.

E. SARIN (*Biochem. Z.*, 1921, **120**, 259—264).—The addition of acids to the sugar syrups used for feeding bees exerts a harmful effect on the biochemical processes of the formation and ripening of honey.

H. K.

Citric Acid Content of Milk and Milk Products.

G. C. SUPPLEE and B. BELLIS (*J. Biol. Chem.*, 1921, **48**, 453—461).—From a series of estimations, it is shown (1) that the citric acid content of milk from different cows on the same ration shows a marked variation, (2) that there is no loss of citric acid during the process of drying or concentrating milk, (3) that the citric acid content decreases during ageing in the presence of highly developed acidity (cf. Sommer and Hart, A., 1918, i, 465).

E. S.

Day and Night Urine during Complete Rest, Laboratory Routine, Light Muscular Work, and Oxygen Administration.

JAMES ARGYLL CAMPBELL and THOMAS ARTHUR WEBSTER (*Biochem. J.*, 1921, **15**, 660—664).—The night urine contained always less total nitrogen, more ammonia, less creatinine, urea, uric acid, and amino-acids, and was more acid than during the day. The phosphate tide is considered to be due to the increased acidity, which in its turn is attributed to delayed excretion of certain fixed acids, formed in the cells during the day. The sulphur was evenly distributed between the day and the night. Administration of 33–40% oxygen did not affect the composition of the urine.

G. B.

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Viscometric and Stalagmometric Measurements of Urine. ERNST JOËL (*Biochem. Z.*, 1921, **119**, 93—107).—The viscosity of normal urine is 1.0 to 1.05. The presence of colloidal materials has a considerable influence on this value. H. K.

Which Carbohydrates are excreted in the Urine of Sucklings when the Sucrose in the Food Exceeds the Assimilation Limit? A Method for the Quantitative Estimation of several Carbohydrates simultaneously in the Urine. HANS MURSCHHAUSER (*Biochem. Z.*, 1921, **119**, 328—338).—Experiments with babes under one year of age showed that sucrose administered in excess of the assimilation value appeared in the urine, partly unchanged and partly as dextrose and levulose. The three sugars are estimated by determining the rotation and reducing power before and after inversion. H. K.

Alkapton Chromogen. G. KATSCH and GÉZA NÉMET (*Biochem. Z.*, 1921, **120**, 212—217).—The ethereal extract of an alkapton urine poured on to unburnt lime acquires an evanescent vivid blue colour. The reaction is very sensitive. The urine of many individuals, after administration of homogentisic acid, slowly darkens, but homogentisic acid is not detectable. The supposed derivatives of this acid which give rise to this reaction are called alkapton chromogens. H. K.

Chemistry of Diabetic Glycosuria. AL. IONESCU (*Bul. Soc. Chim. România*, 1921, **3**, 97—104).—A theoretical paper, suggesting that glycosuria is due to a disturbance of the normal equilibrium between the diastatic reactions occurring in the blood. Thus, excessive hydrolytic action would result in the formation of considerable quantities of acids, ketones, and aldehydes, in the disposal of which the alkalinity of the blood would assist, but these would probably be chiefly converted into dextrose in quantities greater than could be dealt with by the liver. The blood would be affected in regard to the distribution of electrolytes between the white corpuscles and the serum, and, as a consequence, the activity of the liver in converting dextrose into glycogen would be diminished. J. K.

The Types of Reaction of the Bile Pigments and the Quantitative Relation of Bilirubin to Cholesterol in the Blood during different Forms of Jaundice. F. ROSENTHAL and K. MEIER (*Arch. exp. Path. Pharm.*, 1921, **91**, 246—271).—The forms of jaundice investigated were mainly experimental. In each case the type of diazonium reaction (cf. van den Bergh and Muller, A., 1917, ii, 58) given by the serum was determined and the cholesterol content of the latter estimated. The readiness with which bilirubin appears in the urine in each case was also noted. E. S.

The Theory of Narcosis. I. TRAUBE and P. KLEIN (*Biochem. Z.*, 1921, **120**, 111—124).—The authors have examined the Tyndall effect and the ultramicroscopic behaviour of aqueous solutions

of a number of organic substances of slight or moderate solubility and find that some substances show two widely differing degrees of dispersity. Stalagmometric experiments on these show that the higher the dispersity the greater the effect on the surface tension of water. The results show that other factors besides those postulated in Traube's theory of narcosis must play a part, for the hydrocarbons and alkyl haloids have little effect on the surface tension and yet are powerful narcotics. H. K.

The Effective Strengths of Narcotics. I. Experiments on the Isolated Frog's Heart. H. FÜHNER (*Biochem. Z.*, 1921, 120, 143—163).—The isonarcotic concentration of 40 narcotics has been determined on the isolated frog's heart and the drop numbers have been compared, by means of Traube's stalagmometer. Alcohols and their derivatives, paracetaldehyde, acetone, and ethyl ether have a marked effect on the surface tension. Esters are less active, but benzene and many alkyl haloids are inactive even in saturated solution. Apart from the alcohols and related derivatives, there is no correspondence between narcotic action and depression of surface activity as postulated by Traube's theory. The narcotic concentrations, however, show a parallelism with the aqueous solubility in salt solutions. H. K.

The Action of some Derivatives of Chloroform with Special Reference to Traube's Theory of the Action of Narcotics of the Aliphatic Series. GEORG JOACHIMOGLU (*Biochem. Z.*, 1921, 120, 203—211).—Traube's theory of narcosis is untenable. Among the chloro-derivatives of methane and ethane or ethylene, the narcotic action and surface activity are by no means parallel. H. K.

Barium Chloride Poisoning. AL. IONESCU (*Bul. Soc. Chim. România*, 1921, 3, 94—97).—Investigation of a number of recent fatal cases of poisoning due to barium chloride confirms the observations of Ogier and others that a very small proportion of the fatal dose is discoverable in the organs, positive results being only obtained by the Flandin-Danger method, and not by a combination of dialysis with the Fresenius-Babo process. It is suggested that it will be advisable in such cases to examine the bones, since these appear to take up the overwhelming proportion of the poison. The action of this is attributed, in agreement with previous workers, to irritation of the neuro-motor system. J. K.

Toad Venom. HEINRICH WIELAND (*Sitzber. bayer. Akad. Wiss.*, 1920, 329—343).—The formulae given to bufotalin and some of its derivatives by Wieland and Weil (A., 1913, i, 1343) must be changed, since it is found that bufotalin retains organic solvents of crystallisation most energetically. Bufotalin crystallised from alcohol is not $C_{16}H_{24}O_4$, but $C_{26}H_{36}O_6 \cdot C_2H_6O$ (which has the same percentage composition). Crystals from ethyl acetate melt at 154° and have the composition $2C_{26}H_{36}O_6 \cdot C_4H_8O_2$. The solvent is given off slowly in a high vacuum at 150° , and on careful heating in a high vacuum at 225 — 230° bufotalin sublimes. Of the six

oxygen atoms, two are present as a lactone group, two as an acetyl group, and two are hydroxylic. Of the latter groups, one is capable of acetylation, which yields *acetyl bufotalin*, $C_{28}H_{38}O_7$, m. p. 254° , and the other can be oxidised to a ketone group, present in *bufotalone*, $C_{26}H_{34}O_6$, m. p. 261° . Bufotalin is reduced by palladium black and hydrogen to *tetrahydrobufotalin*, $C_{26}H_{40}O_6$, m. p. $204-205^\circ$. Bufotalin, formed by the action of concentrated hydrochloric acid on bufotalin, is $C_{24}H_{30}O_3$ (not $C_{16}H_{20}O_2$, as previously supposed). In its formation one molecular proportion of acetic acid and one of water are removed from bufotalin. Bufotalin melts at $222-223^\circ$ and is yellow in colour. It is reduced catalytically by palladium to colourless *bufotalan*, $C_{24}H_{32}O_3$, m. p. $198-199^\circ$, and hence contains four double bonds. Unlike its precursors, bufotalan does not give Liebermann's cholesterol reaction with acetic anhydride and sulphuric acid.

The carbon skeleton of bufotalin (apart from the acetyl group) is derived from a saturated hydrocarbon, $C_{24}H_{42}$, with eight hydrogen atoms less than the corresponding aliphatic one. Hence bufotalin contains four carbon rings. Now the bile acids are also derived from a complex, C_{24} , with four rings, and, as was shown by Windaus and Neukirchen (A., 1920, i, 41), cholesterol differs from the bile acids by an additional *isopropyl* group at the end of a side-chain, $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHMe-$, which in cholic acid is represented by $CO_2H \cdot CH_2 \cdot CH_2 \cdot CHMe-$. Wieland considers it very probable that in bufotalin this side-chain is further oxidised to a γ -lactone, $CH_2 \cdot CMe > O$, and the chief problem at present is to convert $CH_2 \cdot CO > O$, and the chief problem at present is to convert bufotalan, $C_{24}H_{32}O_3$, into cholanolic acid, $C_{24}H_{40}O_2$, the parent substance of the bile acids.

A second crystalline toxic substance from the skin of the toad, previously called bufotalin by Wieland and Weil, is now named *bufotalidin*, $C_{26}H_{36}O_7$, probably oxybufotalin. With alcohol of crystallisation, it melts at 175° and after heating in a high vacuum at $228-230^\circ$.

Bufagin, the venom of the tropical toad *Bufo aqua*, isolated by Abel and Macht (A., 1912, ii, 1193), is certainly not identical with bufotalin, and according to Faust, has only one-tenth of the physiological action of the latter. Wieland is not convinced that the molecular weight of bufagin has been correctly determined, and considers that Abel and Macht's formula, $C_{18}H_{24}O_4$, may require alteration to $C_{27}H_{38}O_6$, which is that of a methyl ether of bufotalin.

[The above toad venoms are heart poisons and pharmacologically similar to digitalis and strophanthus. Digitoxigenin is, according to Cloetta (A., 1921, i, 39), $C_{24}H_{36}O_4$, and strophanthidin (cynarinogenin, A., 1915, i, 704) has 23 or possibly also 24 carbon atoms. All these heart poisons from various animal and vegetable sources seem to be related to cholesterol and the bile acids.] G. B.

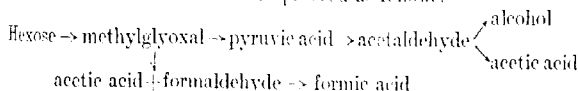
Chemistry of Vegetable Physiology and Agriculture.

The Effect of Hydrogen-ion Concentration on the Production of Carbon Dioxide by *Bacillus butyricus* and *Bacillus subtilis*. MATILDA MOLDENHAUER BROOKS (*J. Gen. Physiol.*, 1921, 4, 177—186).—The rate of production of carbon dioxide by *Bacillus butyricus* and *Bacillus subtilis* is a maximum at P_H 7 and 6·8 respectively. If alkali be added to the culture at its optimum P_H recovery in the rate of production takes place; if acid be added, recovery takes place only if the amount added be small and if it be neutralised by an equivalent amount of acid. W. O. K.

Bacteria as a Source of the Water-Soluble B-Vitamin. SAMUEL R. DAMON (*J. Biol. Chem.*, 1921, 48, 379—384).—Feeding experiments on rats indicate that *B. paratyphosus*, *B. B. coli*, and *B. subtilis* do not produce vitamin-B (cf. Pacini and Russell, A., 1918, i, 329). E. S.

Characteristics of certain Pentose-destroying Bacteria, especially as Concerns their Action on Arabinose and Xylose. E. B. FRED, W. H. PETERSON, and J. A. ANDERSON (*J. Biol. Chem.*, 1921, 48, 385—411; cf. A., 1920, i, 406, 513, 911).—Pure cultures of twelve strains of lactic acid bacteria were isolated from corn silage and sauerkraut. They are classified in two main divisions, according as they ferment levulose with or without the production of mannitol, further subdivision depending on their fermentative ability towards various sugars. The fermentation of arabinose and xylose by these bacteria results in the formation of acetic acid, lactic acid, and carbon dioxide. The two acids are formed in approximately equimolecular proportions, the main line of fermentation being, apparently, simple cleavage into acetic and lactic acids. The mannitol-forming bacteria also slowly ferment lactic acid to acetic acid and carbon dioxide. E. S.

The Attack of Dextrose and Lævulose by the Pyocyanic Bacillus. E. AUBEL (*Compt. rend.*, 1921, 173, 1493—1495).—Amongst the products of the decomposition of dextrose and lævulose by the pyocyanic bacillus, alcohol, acetic acid, and formic acid have invariably been found. Lactic acid has also been found as a by-product from levulose. The degradation of the two hexoses under these conditions is considered to proceed as follows.



W. G.

Action of Acids on Fermentation by Yeast. R. SOMOGYI (*Biochem. Z.*, 1921, 120, 100—102).—Acids exert a harmful effect on fermentation by yeast. This is proved by the examination of

the action of thirteen acids, organic and inorganic, at concentrations between $N/6$ and $N/1500$. The inhibitory action does not appear to be solely dependent on the hydrogen-ion concentration, but on other physical properties as well. H. K.

The Change undergone by Nitrogenous Substances in the Final Phases of Yeast Autolysis. NICOLAUS N. IVANOV (*Biochem. Z.*, 1921, 120, 1—24; cf. A., 1918, i, 365).—If, after yeast autolysis has proceeded for some time the solution be made alkaline, the ensuing autolysis is accompanied by an increase of protein nitrogen (as estimated by Stutzer's method), at the expense of the original protein decomposition products which are precipitable by lead acetate and phosphotungstic acid. The amino-nitrogen, however, as determined by Van Slyke's method, is unchanged. If the autolysis in alkaline solution is allowed to continue at a higher temperature, for example, 60° , there is a loss of amino-nitrogen unaccompanied by any increase of protein-nitrogen. This is interpreted as being due to the formation of humin-like substances at the expense of the amino-acids of the autolysate and carbohydrates. H. K.

The Influence of Fermentation Products on the Decomposition of Proteins in Yeast. NICOLAUS N. IVANOV (*Biochem. Z.*, 1921, 120, 62—80).—During the process of fermentation substances are formed which inhibit the decomposition of protein. It is shown experimentally that the inhibition is the result of two factors, (1) production of alcohol during fermentation, (2) development of acidity; the former plays the greater rôle. H. K.

Protein Decomposition in Yeast during Fermentation. NICOLAUS N. IVANOV (*Biochem. Z.*, 1921, 120, 25—61).—Stutzer's method (*J. Landw.*, 1880, 28, 103) for the estimation of proteins in solutions by precipitation with cupric hydroxide does not differentiate between proteins and humins. During the fermentation of sugar by yeast there is decomposition of protein, earlier statements to the contrary being based on results obtained by Stutzer's method, the humins formed being stable to the proteolytic enzymes present and compensating for the loss of protein. Meyer's "excrements of fermentation" are probably humin-like substances. H. K.

Effect of certain Stimulating Substances on the Invertase Activity of Yeast. ELIZABETH W. MILLER (*J. Biol. Chem.*, 1921, 48, 329—346).—The addition of an alcoholic or aqueous yeast extract to growing yeast is known to stimulate both growth and formation of invertase. It is now shown that these two effects are produced by different substances, a partial separation of which may be effected by removal of the growth stimulant by extraction with benzene, adsorption with Fuller's earth, or precipitation with phosphotungstic acid. The substance accelerating invertase formation is also contained in high concentration in a gummy precipitate which separates from alcoholic extracts of yeast. Its action is not of the nature of a co-enzyme, since it is without influence on

invertase itself; moreover, although Abderhalden and Schaumann (A., 1919, i, 108) found that yeast extract increased the invertase activity of both dried yeast and maceration juice, the increase was so small as to fall within the limits of experimental error. Extracts of wheat germ also stimulate growth but do not increase the invertase concentration in yeast. E. S.

The Lactase Content and the Fermenting Power of Lactose-fermenting Yeasts. RICHARD WILLSTÄTTER and GERTRUD OPPENHEIMER (*Z. physiol. Chem.*, 1922, **118**, 168—188).—Lactase can be obtained from fresh yeast without previously destroying the cell, providing that the acidity is neutralised. The lactose-splitting activity of yeasts, sometimes even of the same strain, varies within very wide limits. In some cases lactose is fermented more quickly than an equivalent mixture of dextrose and galactose. It is also shown that in certain cases the fermentation of lactose proceeds almost as quickly as, or perhaps more quickly than, the hydrolysis of the disaccharide. When the fermentation is interrupted in such cases no monosaccharides are found in the fermenting medium. This differs from the mechanism of the fermentation of sucrose, when hydrolysis takes place almost immediately. It is concluded that lactose-fermenting yeasts can ferment that sugar without hydrolysing it and therefore contain a lactose-*zymase*. S. S. Z.

Vitamin Requirements of certain Yeasts and Bacteria. CASIMIR FUNK and HARRY E. DUBIN (*J. Biol. Chem.*, 1921, **48**, 37—443).—By shaking autolysed yeast with either Fuller's earth or "norit" vitamin-B is completely removed; the filtrate, however, still promotes the growth of yeast. The authors conclude that a hitherto unknown vitamin, for which the name vitamin-D is suggested, is present in yeast. E. S.

The Rôle of Acetaldehyde in Alcoholic Fermentation. A. FERNBACH and M. SCHOEN (*Bull. inst. Pasteur*, 1920, **18**, 385—406).—A review of the present state of knowledge of the subject, with special reference to the work, already published, of Neubauer and Fromherz, Neuberg and others, Mazé and Lintner, Liebig, J. B. Dumas, Connstein, Leudeke, and the authors.

CHEMICAL ABSTRACTS.

The Lipase of *Aspergillus niger* (van Tiegh). ROBERT SCHENKER (*Biochem. Z.*, 1921, **120**, 164—196).—A pure culture of *Aspergillus niger* (identical with Brenner's β -strain) showed growth on various glycerides, especially triacetin, but no growth on ethyl esters. The lipase present can be extracted, with water or glycerol, in the form of a press-juice, or as a stable acetone-treated preparation. Fatty media favour the development of the enzyme more than media containing glycerol or sucrose. The optimum temperature for the enzyme is 40°, and the optimum reaction of the solution, for its activity, neutral or weakly acid. H. K.

The Toxicity of Different Nitrophenols towards *Aspergillus niger*. L. PLANTEFOL (*Compt. rend.*, 1922, **174**, 123—126).—Phenol and its nitro-derivatives are toxic towards *Aspergillus niger*, the nitro-derivatives being more toxic than phenol itself. Of the three mononitrophenols, the ortho is the least and the para the most toxic. 2:4-Dinitrophenol is one hundred times more toxic than phenol and ten times more toxic than the most toxic mononitrophenol. 2:4:6-Trinitrophenol is about as toxic as *m*-nitrophenol. W. G.

Bactericidal Action of the Quinones and Allied Compounds. GILBERT THOMAS MORGAN and EVELYN ASHLEY COOPER (*Biochem. J.*, 1921, **15**, 587—594).—When proteins are added to solutions of *p*-benzoquinone, the latter slowly disappears and quinol can be detected; the quinone seems to react as a peroxide and differs fundamentally from phenols, which are merely protein precipitants. *p*-Benzoquinone is 80—190 times as effective in destroying *B. typhosus* as quinol or phenol. In ascending a homologous series, the quinones become less, the phenols more bactericidal; thymoquinone is less effective than thymol. The authors incline to the view that the high bactericidal power of benzoquinone is connected with the interaction of nascent peroxide molecules with the bacterial protoplasm. G. B.

Theory of Disinfection. I. TRAUBE and R. SOMOGYI (*Biochem. Z.*, 1921, **120**, 90—99).—Experiments with *Staphylococcus* and *Bacillus coli* show that apart from disinfectants of the type of potassium permanganate and hydrogen peroxide, which act chemically, physical forces are the deciding factor, such as surface activity, adsorption, flocculation, and other properties. H. K.

P_H Again. I. TRAUBE (*Biochem. Z.*, 1921, **120**, 108—110).—The author's contention is that P_H is too much in the foreground to the exclusion of other factors. H. K.

Conditions for the Biological Action of Röntgen Rays. I. EUGEN PETRY (*Biochem. Z.*, 1921, **119**, 23—44).—The inhibitory action of Röntgen rays on the growth of seeds could not be influenced by temperature changes, lack of oxygen, or by the presence of potassium cyanide. The action is therefore not connected with the respiratory processes. The small temperature coefficient points to the action being photochemical. H. K.

The Action of Bases and Salts on Biocolloids and Cell Masses. D. T. MACDOUGALL (*Proc. Amer. Phil. Soc.*, 1921, **60**, 15—30).—A study of the swelling of biocolloids in dilute salt solutions in connexion with the suggestion that the chief effect of salts in nutrient solutions is in restricting, limiting, or defining the hydration of the cell colloids. Hydroxides of the metallic bases were found to decrease the swelling of plates of agar in the order: calcium, potassium, sodium, in concentrations of 0.01 molar. The chlorides show the same relative action. Hydration of agar is increased by

the hydroxides of these metals at 0.001*N*, but no well-defined differences between the metals could be observed. Similar effects were produced by chlorides of calcium, magnesium, potassium, and sodium at 0.0001*M*, and potassium and sodium at 0.001*M*. The purified agar used in the experiments has a p_H value of 6.5 and swells more in hydrochloric acid of p_H 4.2 than in pure water. The p_H range over which large swelling of the agar occurs is from 4.2 to 11. It also swells largely in 0.0001*M* sodium and potassium nitrates, but not in the sulphates. Similar measurements were also made on the swelling of gelatin. The gelatin used had a p_H value of 5.2 and it was noted that both hydrogen and hydroxyl ions caused increasing swelling with reference to the isoelectric point, at which minimum swelling occurred. The swelling in 0.0001*M* potassium chloride ($p_H=5.7$) was not much greater than in water; the swelling in potassium chloride 0.001*M* ($p_H=5.8$) is about double that in water. Calcium chloride solutions induce maximum swelling at 0.001*M*, but depress hydration as the concentration increases or decreases from 0.001*M*. The interest of these results lies in the fact that a mixture of a vegetable mucilage (pentosan) type of colloid with a protein colloid exemplifies many of the reactions of living or dead cell masses. Experiments were therefore continued with plates of gelatin 3 : agar 2 parts, and gelatin 2 : agar 3 parts. In the latter, sensitiveness to hydrogen ions was more marked than in the case of agar alone, but the effect of potassium chloride is about the same as that upon agar alone. The mixture in which gelatin predominated showed increase of swelling as p_H was increased to 2.01, whilst potassium chloride showed an effect similar to its effect on agar. The work was then extended to living and dead cell masses, such as sections from the roots of *Zea mays* (dominantly pentosan), which were closely parallel to those of the agar 3 : gelatin 2 mixture. Roots of strawberry showed different hydration reactions depending on whether they were grown in saline soils or in sand, the latter showing greater hydration. Joints of *Opuntia* (dominantly pentosan) showed maximum swelling in 0.01*N*-potassium hydroxide, hydrogen chloride at 0.001*N*, and potassium chloride at 0.0001*M*, all in excess of the swelling in water. The changes in volume of living cell masses in hydrating solutions include osmotic-plasmolytic effects in the alteration of the volume of the included cells. The hydration of dead cell masses includes possible osmotic action of cell-walls.

CHEMICAL ABSTRACTS.

Action of Neutral Salts on Plant Plasma. II. HUGO KAHMO (*Biochem. Z.*, 1921, 120, 125—142). The coagulating action of neutral salts on plant plasma (sections of *Tradescantia virginica*) depends on both ions, the anions playing a greater part than the cations. The coagulating property of anions falls off in the order $CNS > I > Br > NO_3 > Acetate > Cl > Tartrate > Citrate > SO_4$ and of the cations $K > NH_4 > Na > Sr, Mg, Ba, Ca$. The order of the ions is substantially the lyotrope series, but in the reverse order of their action on protein. The possible reasons for this are discussed.

H. K.

The Occurrence and Action of Saccharophosphatase in the Organism of the Plant. ANTONIN NĚMEC and FRANTIŠEK DUCHOŇ (*Biochem. Z.*, 1921, **119**, 73–80).—The sodium and calcium salts of artificially prepared saccharophosphoric acid are hydrolysed with formation of free phosphoric acid by the resting seeds of the higher cultivated plants as well as by the leaves of *Solanum tuberosum*. Aqueous extracts of the seeds have the same power, but to a lesser degree. Alkali is inimical to the action of the enzyme, the optimum acidity being 0.03*N* for saccharophosphatase and 0.004*N* for the autolytic phosphatase of the seeds.
H. K.

Pectic Substances of Plants. II. Preliminary Investigation of the Chemistry of the Cell-walls of Plants. DONALD HERBERT FRANK CLAYSON, FREDERICK WALTER NORRIS, and SAMUEL BARNETT SCHRYVER (*Biochem. J.*, 1921, **15**, 643–653; cf. *A.*, 1917, i, 245).—The authors call *cytopentans* substances related to Schulze's hemicelluloses, which are extracted by cold *N*-sodium hydroxide and then precipitated by addition of alcohol. They are coloured blue by iodine, and do not reduce Fehling's solution until after hydrolysis by acids, when they give 40–85% of pentosans. Cytopentans form a relatively small part of crude pectin, and the name *cytopectic acid* is suggested for the rest. The samples of this acid from six species of plants contained 41.22–42.88% C, 5.31–5.71% H, and 0.15–0.85% ash. [α]_D²⁰ +260° to +280°. The percentage of methyl alcohol set free by sodium hydroxide was 0.16–0.42% (cf. von Fellenberg, *A.*, 1918, i, 215, and Tutin, *A.*, 1921, i, 751).
G. B.

Incrustive Substances of Plants. II. ERICH SCHMIDT and FRANZ DUYSEN (*Ber.*, 1921, **54**, [B], 3241–3244; cf. *A.*, 1921, i, 912).—The removal of incrusted substances is effected more conveniently by means of a solution of chlorine dioxide in acetic acid (50%) than by alternate treatment with chlorine peroxide and sodium sulphite; the method has the advantage that the attacked incrustations remain dissolved in the acid. Subsequently, the presence of polysaccharides which give a blue coloration in the tissues can be demonstrated readily by means of zinc chloride-iodine solution which gives untrustworthy results in the presence of the incrustations. The simple manipulation required and the stability of the solutions render the chlorine dioxide-acetic acid valuable for micro-chemical investigations. The reagent causes the cell-walls to swell slightly, but this action occurs so uniformly that the anatomical features of the plant are not altered thereby.
H. W.

The Detection of the Pseudo-bases of Anthocyanidins in Plant-tissues. RAOUL COMBES (*Compt. rend.*, 1921, **174**, 58–61).—The substances characterised by Noack in the amyl alcohol extracts of leaves of *Polygonum compactum* and *Ampelopsis hederacea* and the pericarps of *Arsculus hippocastanum* as anthocyanidin pseudo-bases (cf. *Z. Botanik*, 1918, **10**, 561) were probably

phlobatannins and the red substances he obtained by the action of acids which he considered as anthocyanidins were probably phlobaphens. The author does not consider that Willstätter's method for the separation of anthocyanidins and anthocyanins by means of amyl alcohol can be applied to the detection of pseudo-bases of anthocyanidin in plant-tissues. It is necessary to extract the pigments and characterise them by examining the pure products to obtain conclusive results.

W. G.

Effect of Temperature and of the Concentration of Hydrogen Ions on the Rate of Destruction of Antiscorbutic Vitamin (Vitamin-C). H. C. SHERMAN, V. K. LA MER, and H. L. CAMPBELL (*Proc. Nat. Acad. Sci.*, 1921, 7, 279—281).—Guinea pigs were used and both the survival period and post-mortem findings were taken into account in estimating activity of solutions. Boiling tomato juice (P_H 4.3) for one hour destroyed 50%, for four hours 68%; the curve is much flatter than for a unimolecular reaction. The temperature coefficient for 10° between 60° and 80° was 1.23, between 80° and 100° , 1.12. Partial neutralisation or making alkaline causes the vitamin to be destroyed at a somewhat greater rate. Ninety to ninety-five % is destroyed in five days even at 10° , at an alkalinity of only $P_H=9$ (cf. Delf, A., 1920, i, 460).

G. B.

Occurrence of a Crystalline Tannin in the Leaves of the *Acer ginnala*. ARTHUR GEORGE PERKIN and YOSHISUKE UYEDA (*T.*, 1922, 121, 66—76).

Barbassu Nuts. HENRI JUMELLE (*Mat. grasses*, 1921, 13, 578—587).—The nuts (genus *Orbignia*) contain: Water 4.21%, oil 66.12%, carbohydrates 14.47%, protein 7.18%, cellulose 5.99%, ash 2.03%. The oil has the following constants: m. p. 26° , solidification point, 22.7° , saponification number, 247.7, ether number, 242.9, iodine number, 16.83, Reichert-Meißl number, 6.2, Polenske number, 11.3, glycerol 13.2%. The cake has the following composition: Water 11.59, oil 6.50, proteins 19.81, carbohydrates 40, cellulose 16.50, ash 5.60%. (CHEMICAL ABSTRACTS.)

Application of Bourquelot's Biochemical Method to some Members of the *Caryophyllaceae* and *Papilionaceae*. CHARLES VERGELOT (*Bull. Soc. chim. Biol.*, 1921, 3, 513—519).—By the successive action of invertase and emulsin on plant extracts, and observation of the rotation and reducing power, the author concludes that *Stellaria holostea* contains sucrose, but *Saponaria officinalis*, *Genista sagittalis*, *Eryum hirsutum*, and *Anthyllis vulneraria* contain other unknown sugars. Glucosides are indicated in most cases, and their extraction might be attempted from *Genista sagittalis*, *Eryum tetraspermum*, and *Saponaria officinalis*. G. B.

The Food Relations of *Fusarium lini*. YOSHIHIKO TOCHINAI (*Ann. Phytopath. Soc. Japan*, 1920, 4, 22—33).—The fungus utilises carbohydrates as sources of carbon in the following descending order: inulin, dextrose, maltose, arabin, soluble starch, levulose,

galactose, sucrose, and lactose. As indicated by the growth made, organic acids as sources of carbon are unfavourable to the fungus; the descending order of utilisation is as follows: succinic, malic, citric, fumaric, maleic, and racemic acids. *d*-Tartaric acid is more readily assimilated than *l*-tartaric acid. Mannitol, but not glycerol, is a favourable source of carbon. Phenol derivatives prevent growth. Organic nitrogen compounds, particularly amides, are far better sources of nitrogen than inorganic compounds.

CHEMICAL ABSTRACTS.

Hazel-nut oil and the Estimation of Arachidic acid. J. PRITZKER and R. JUNGKUNZ (*Z. Unters. Nahr. Genussm.*, 1921, **42**, 232—241).—The following characters were given by two samples of hazel-nut oil prepared in the laboratory: d_{20}^{25} 0.9152, 0.9156; n_D^{20} 1.472, 1.474; acid number 0.8, 1.7; saponification number 191.8, 189.1; iodine number (Hanus) 83.8, 85.4; Reichert-Meissl number 1.54; Polenske number 0.5; unsaponifiable matter 0.58%. Thorough investigation showed that there was no arachidic acid present. The following acetone method was used for the estimation of arachidic acid: 20 grams of the oil were saponified with 40 c.c. of 20% potassium hydroxide, and the clear solution was diluted with 50 c.c. of hot water and 20 c.c. of 25% hydrochloric acid were added. After fifteen minutes, the fatty acids were separated and dissolved in 180 c.c. of boiling acetone. Twenty c.c. of *N*-aqueous potassium hydroxide were added and the solution was allowed to cool and kept at 15° for half an hour. The crystals obtained were washed several times with small quantities of acetone, dissolved in water, the fatty acids liberated with hydrochloric acid, and dissolved by warming with 50 c.c. of 90% alcohol. The solution was slowly cooled and left for three hours at 15°. If arachidic acid is present, the precipitate consists of fine laminae. It is filtered, washed three times with 10 c.c. of 90% alcohol, and transferred to a weighed flask by dissolving in boiling alcohol. The alcohol is evaporated and the residue dried at 100° and weighed. Crude arachidic acid has m. p. 72—75°. If the m. p. is below 70°, the residue must be again recrystallised from 90% alcohol and reweighed. The quantity obtained is corrected for its solubility in 90% alcohol. This method does not require large quantities of alcohol and ether, and the troublesome manipulation of the lead soap is avoided. Schädler and Knorr's colour reactions for hazel-nut oil are found to be untrustworthy.

H. C. R.

The Chemical Constituents of some *Loranthaceae*. D. H. WESTER (*Rec. trav. chim.*, 1921, **40**, 707—723).—Leaves of *Loranthus pentandrus*, *L. globosus*, *L. atropurpureus*, and *Viscum album* were examined with respect to their chemical constituents. The ash of the leaves was determined and also the percentage of manganese in the ash, figures for the latter being rather high. From the first two species a glucoside identical with quercitrin was isolated, although its properties were not in all respects identical with those

previously described. The author states that a previous specimen of quercitrin prepared by him showed similar discrepancies, m. p. being 174—176°, not 182—185°, and the benzoate has m. p. 187—189°, not 239°, whilst the author's specimens recombine with water of crystallisation which is lost on heating and the solubility in 95% alcohol is 1 part in 70.5 parts, not 1 in 229.

The m. p. of quercitrin from *Loranthus* is lowered as the substance is purified. Its solubility in various solvents is described qualitatively and, in some cases, quantitatively. Three reactions are given which serve to distinguish quercitrin from quercetin: with ferric chloride and ether, the latter gives characteristic colours, the former no reaction; with zinc and hydrochloric acid in presence of amyl alcohol, the former gives a red coloration after some hours, the latter a yellow tint; with a soluble silver salt, the former gives no reaction, the latter a red coloration which turns blue and finally gives a black precipitate of metallic silver. The last test is stated to confirm the formula for quercitrin suggested by Perkin and Everest ("The Natural Colouring Matters," 1918). The brown coloration given by both substances on boiling with ferric chloride is due to separation of colloidal ferric hydroxide. Quercetin has $d_{1.6}$; that of quercitrin is lower.

The glucoside sugar consists entirely of rhamnose. Wax from *Loranthus* species is complex; the only constituent definitely identified is melissic alcohol, but this was not found in *L. atropurpureus*, neither was quercitrin obtained from this species. *Fiscum album* does not contain invertase, reductase, amylase, emulsin, tannin, nor glucoside; however, xanthophyllin and a volatile alkaloid were obtained, but the experience of previous workers that it is difficult to extract pure substances from this species is confirmed.

H. J. E.

The Presence of Sucrose and Aucubin in the Seeds of *Melampyrum arvense*, L. MARC BRIDEL and (MILLE) MARIE BRAECKE (*Compt. rend.*, 1921, 173, 1403—1405; cf. A., 1921, i, 840).—The presence of a glucoside in the seeds of *Melampyrum arvense*, decomposable by emulsin giving a black product has previously been indicated (*loc. cit.*). Aucubin has now been extracted in definite crystalline form from these seeds, and sucrose has also been isolated. Ludwig and Muller have isolated a glucoside from these seeds (cf. *Archiv Pharm.*, 1872, 199, 6), which they considered to be identical with rhinanthin obtained from the seeds of *Rhinanthus Crista-Galli*, L. (*Archiv Pharm.*, 1870, 192, 199), but the authors consider further work is necessary to establish the identity or otherwise of aucubin and rhinanthin.

W. G.

The Changes which Oranges Undergo on Keeping. G. ANDRÉ (*Compt. rend.*, 1921, 173, 1399—1401).—When oranges, cut in halves, are kept under sterile conditions they undergo a slight loss in weight, which is accompanied by a marked loss in acidity and a slighter diminution in sugar content together with inversion of some of the sucrose. These changes are not entirely

due to oxidation, as they proceed to a less extent in a vacuum. It is probable that there is also some diastatic action. W. G.

Presence in Several Indigenous Orchids of Glucosides yielding Coumarin on Hydrolysis. H. HÉRISSEY and P. DELAUNEY (*Bull. Soc. Chim. Biol.*, 1921, 3, 573—579).—A glucoside yielding coumarin on hydrolysis by dilute sulphuric acid or by emulsin is contained in the following three species of orchids: *Orchis purpurea*, Huds., *O. Simia*, Lam., *O. militaris*, L. (cf. Bourquelot and Hérisséy, A., 1920, i, 586). This glucoside is not identical with loroglossin (Bourquelot and Bridel, A., 1919, i, 243; Delaune, A., 1920, i, 801, and A., 1921, i, 296), which does not yield coumarin on hydrolysis. E. S.

Occurrence of Ellagic Acid in *Rubus Idaeus*. The Cause of the Clouding of Raspberry Juice. HERMANN KUNZ-KRAUSE (*Arch. Pharm.*, 1921, 259, 193—206).—Raspberry juice on keeping becomes cloudy owing to the deposition of a small quantity of a microcrystalline substance, the formation of which is accelerated by the addition of small quantities of a mineral acid. This deposit was collected, and decolorised and purified by warming in sodium hydroxide solution with hydrogen peroxide, and reprecipitating with acetic acid, and was identified as ellagic acid by analysis of its pyridine compound, $(C_{11}H_8O_8 \cdot H_2O) \cdot 2C_5H_5N$, and by characteristic reactions with alkali hydroxides, ferric chloride, nitrous acid, etc. The ellagic acid does not apparently exist as such in the fruit itself or initially in the fruit juice, but originates from a molecular complex of a higher order such as a tannoid or, possibly even, from the red colouring matter of the fruit. G. F. M.

Water-soluble Colouring Matters of the *Schizophyceae*. KARL BORESCH (*Biochem. Z.*, 1921, 119, 166—214).—The aqueous extracts of the water-soluble colouring matters of pure cultures of numerous species of *Schizophyceae* were examined spectrophotometrically. Phycocyan, a blue colouring matter with a maximum absorption between the C and D lines, occurred alone in some species, in others mixed with phycoerythrin, a red colouring matter with an orange-yellow fluorescence and an absorption maximum in the green between the lines D and E. The latter pigment also occurred singly in certain species. When mixed, the two pigments were separable by capillary analysis. H. K.

Sakoa Oil from Madagascar. HENRI JUMELLE (*Mat. grasses*, 1921, 13, 5854—5855).—Sakoa is the name given to *Sclerocarya caffra*. The fruits are drupes and have an acid pulp owing to the presence of citric acid. The seeds contain 56% of oil having the following constants: d_{40}^{20} 0.9167, n_D^{40} 1.460, saponification number 193.5, iodine number 76.6, Reichert-Meißl number 0.1, Polenske number 0.45, unsaponifiable matter 0.6%, m. p. of fatty acids 25°. The oil is non-drying. CHEMICAL ABSTRACTS.

Alcohol-soluble Protein of the Caryopsis of *Sorghum vulgare*. I. Extraction and Identification. SABATO VISCO (*Arch. Farm. speriment. Sci. aff.*, 1921, **31**, 173—176).—Hot 70% aqueous alcohol extracts from the ground caryopsis of *Sorghum vulgare* about 3.5% of a nitrogenous substance, which is named *sorgein* and is classified with the prolamines. It gives the principal colour reactions of the proteins, but not the Adamkiewicz or the Liebermann reaction. In the isolation of the compound, two fractions were obtained which contain respectively 11.19% and 13.61% of nitrogen and may be different compounds. T. H. P.

The Biochemistry of Tobacco. II. Tobacco Seeds. G. PARIS (*Bot. tec. [R. ist. sci. sper. tabacco, Scafati]*, 1920, **17**, 101—115; cf. A., 1917, ii, 227).—The entire seed contains: water, 9.17%; crude protein, 21.87%; fat, 37.68%; amides and sugar, 6.05%; pentosans, 2.9%; cellulose, 7.15%, and ash, 3.84%. The ash contains SO_3 , 1.97%; P_2O_5 , 22.12%; Na_2O , 3.48%; K_2O , 28.5%; CaO , 9.54%; MgO , 14.63%. A sample of oil from Kentucky tobacco seed had d_{40}^{20} 0.9408; temperature of solidification, 12° ; acid number, 4; saponification number, 196; iodine number, 132.8; ether number, 192. The oil consisted of about 52.4% of olein, 22.1% of linolein, and 23.9% of palmitin. No nicotine was found in tobacco seed, except in slight quantities in the germinating seed. The dry, fat-free seed contained 6.5% of total nitrogen, 3.76% of protein nitrogen, 2.39% of nucleic nitrogen, and 0.35% of non-protein nitrogen. The presence of arginine was established. CHEMICAL ABSTRACTS.

Hesperidine-like Substances in the *Umbelliferae*. HAROLD NILSSON (*Svensk Farm. Tidskr.*, 1921, **25**, 233—238).—The paper gives a brief résumé of the chemistry, properties, and tests for hesperidine. Microscopic sections are best made after fixing with acetic acid and freezing. Microscopically the alkaloid is detected as spherocrysts and sheaves. These are soluble in pyridine and quinoline. Seventy specimens were examined; either the spherocrysts or sheaves were noted in the leaves and stems of the following: *Angelica archangelica*, *A. atrapurpurea*, *A. decurrens*, *A. itoralis*, *A. silvestris*, *Achusa cynapium*, *Beton galbanum*, *Conium maculatum*, *Ferula communis*, *F. neapolitana*, *F. scorodosma*, *Imperatoria ostruthium*, *I. hispanica*, *Libanotis siberica*, *Ligusticum scoticum*, *Sesili glaucum*, *S. tenuifolium*, *Trinia vulgaris*. The presence of the alkaloid was also confirmed by chemical tests. In the fourth, sixth, and eighth there was also a positive test for the fruit. CHEMICAL ABSTRACTS.

Action of Coal Gas on Plants. C. WEHNER (*Bied. Zentr.*, 1921, **50**, 425—428).—The author has examined the effect of coal gas on three- to seven-year old trees grown in pots. In winter, the trees are scarcely affected, but in spring they wither and gradually die. Fir and elm trees are especially sensitive, then come maple, whilst lime trees are least sensitive. The trees survive

the action of coal gas in the autumn. From these experiments and further experiments on twigs immersed in water saturated with coal gas it is concluded that the harmful effect of coal gas is most pronounced when the root system commences its activity after winter, and is not due to action on the foliage. The harmful effect is due to certain constituents in the gas, particularly those which impart an odour to the gas. Hydrocyanic acid is particularly harmful.

W. G.

Availability of Organic Nitrogenous Compounds. C. S. ROBINSON, O. B. WINTER, and E. J. MILLER (*J. Ind. Eng. Chem.*, 1921, **13**, 933—936).—It is probable that all amino-nitrogen present in soil in the form of α -amino-acids and a portion of that nitrogen present as acid amides may be added to the class of substances constituting the source of immediately available nitrogen, the chief members of this class being inorganic compounds of ammonia and nitric acid. Peptides may form a class of potentially available compounds; in some cases the peptides in fertilisers are readily hydrolysed to amino-acids and primary and secondary amines.

W. P. S.

Effect of Alum on Silicate Colloids. C. S. SCOFIELD (*J. Washington Acad. Sci.*, 1921, **11**, 438—439).—The removal of soluble salts from certain soils of the western United States by irrigation and drainage leads to serious trouble through the effect of colloidal silicates, principally sodium silicate, on soil texture. By the addition of alum as a dressing insoluble aluminium silicates are formed and sodium sulphate thereby formed is removable in drainage. Analyses of the drainage from soils to which aluminium sulphate had been applied showed that practically all the aluminium had been precipitated by the soil and that equivalent amounts of sodium, calcium, and magnesium had been liberated combined with the sulphate radicle.

G. W. R.

The Flocculation of Soils. II. NORMAN M. COMBER (*J. Agric. Sci.*, 1921, **11**, 450—471).—"Direct" flocculation of the clay soils by salts of iron and aluminium occurs in a manner precisely similar to the coagulation of electro-negative suspensoids by electrolytes. "Indirect" flocculation by neutral salts and some acids results from interaction with the constituents of the clay particle whereby normal flocculating agents are produced. The "abnormal" flocculation of clay by calcium hydroxide is a result of the reaction of lime with the emulsoid surface layer of the clay particle, and does not depend on the formation of calcium carbonate. The difference in the action of flocculating agents on clay and silt particles depends entirely on the relative proportions of emulsoid surface layer to core in the particle. (See also *J. Soc. Chem. Ind.*, 1922, 69A.)

A. G. P.

Organic Chemistry.

The Chemical Nature of Mineral Lubricating Oils. A. E. DUNSTAN and F. B. THOLE (*J. Inst. Petroleum Tech.*, 1921, 7, 417—421).—Mineral lubricating oils appear to contain but a small percentage of paraffin hydrocarbons of the C_nH_{2n+2} series, and consist chiefly of compounds the formulæ of which range from C_nH_{2n} to C_nH_{2n-8} . The olefine contents cannot be determined by extraction with sulphuric acid, as they are thereby converted into condensation products insoluble in the acid. A partial separation of unsaturated hydrocarbons can be achieved by extraction with liquid sulphur dioxide, an oil with an iodine value 46 giving, for example, a residue with iodine value 33 and an extract with iodine value 73. The reaction of mineral oils towards iodine differs profoundly from that of fatty oils, as no constant iodine value can be obtained, an increase in the proportion of reagent to oil invariably augmenting the value. This fact, coupled with the reluctance exhibited to hydrogenation, seems to lead to the conclusion that the unsaturated hydrocarbons in mineral oils consist only to a small degree of true olefines. The saturated compounds are principally naphthenic and probably polynuclear. Solid resinous components containing oxygen are present to the extent of a few parts per cent., and are probably an important cause of "gumming." Removal of these substances, and the more readily oxidisable unsaturated hydrocarbons reduces the gumming tendency, but in oil refining care should be taken not to destroy the more stable unsaturated hydrocarbons, to which the viscosity of the oil is largely due, it having been shown that an increase in viscosity occurs concurrently with a decrease in the hydrogen content.

G. F. M.

The Hydrogenation of Ethylene in Contact with Nickel. ERIC KEIGHTLEY RIDEAL (*T.*, 1922, 121, 309—318).

Bivalent Carbon. ALFRED GILLET (*Bull. Soc. chim. Belg.*, 1921, 30, 329—336).—A theoretical paper in which some evidence is adduced to show the existence of certain bivalent carbon compounds either as unstable intermediate substances or as isomerides of differing degrees of stability.

H. J. E.

The Exchange of Halogen in Unsaturated, Aliphatic Halogenated Hydrocarbons. I. H. P. KAUFMANN (*Ber.*, 1922, 55, [B], 249—267).—It is shown in a variety of ways that the iodine atoms of the stereoisomeric *s*-di-iodoethylenes are removed with much greater difficulty than those of similar saturated aliphatic iodo-compounds. The most probable explanation is that the unsaturated hydrocarbon residue in the immediate vicinity of the halogen atom makes such a complete demand on the affinity

of the latter that but little remains for the attraction of a new atom, whereas the saturated hydrocarbon residue saturates the affinity of the halogen atom less completely and so leaves it more disposed to react with reagents in general.

β. Solid $\alpha\beta$ -di-iodoethylene, m. p. 73° , is conveniently prepared by allowing a solution of iodine in absolute alcohol to remain in contact with acetylene gas under slightly increased pressure and at the atmospheric temperature; the liquid isomeride has b. p. 185° .

A solution of the solid di-iodide in anhydrous ether reacts quantitatively with activated magnesium in accordance with the equation: $C_2H_2I_2 + Mg = C_2H_2 + MgI_2$; in all probability, an unstable organo-metallic compound is formed primarily. Metallic potassium is slowly attacked by a boiling solution of solid di-iodoethylene in anhydrous ether with ultimate production of acetylene and potassium iodide; the formation of $\alpha\alpha$ -di-iodoethylene (see below) during the reaction is established. The latter is prepared more conveniently by allowing the ethereal solution of the solid di-iodide (or more rapidly from the liquid isomeride) to remain in contact with metallic sodium at the atmospheric temperature. It forms colourless crystals which sublime with great ease, m. p. 56° ; the vapours have an extremely unpleasant odour and attack the eyes with great violence. When dissolved in carbon tetrachloride and treated with bromine in direct sunlight, it is transformed into $\alpha\alpha$ -dibromoethylene, yellow leaflets, m. p. 90° , which is thus prepared in the dimeric form, $(C_2H_2Br_2)_2$. If an excess of bromine is used, $\alpha\alpha\alpha\beta$ -tetrabromethane is produced, which is formed also by the further action of bromine on the solid, dimeric dibromide. Similar $\alpha\alpha$ -di-iodoethylene is converted by an excess of chlorine in the presence of bright sunlight into $\alpha\alpha\alpha\beta$ -tetrachloroethane, b. p. 135° , and iodine trichloride. $\alpha\alpha$ -Di-iodoethylene is decomposed by potassium or activated magnesium in the presence of anhydrous ether with quantitative formation of acetylene.

trans- and *cis*- $\alpha\beta$ -Di-iodoethylene and $\alpha\alpha$ -di-iodoethylene are decomposed with liberation of iodine when their ethereal solutions are exposed to ultra-violet light, the velocity of the reaction in the case of the compound first named being approximately twice as great as that in the remaining two cases.

[With F. SCHWEITZER.]—A solution of solid $\alpha\beta$ -di-iodoethylene in anhydrous ether is attacked slowly by zinc ethyl when the mixture is heated until it becomes slightly turbid and subsequently exposed to direct sunlight during several weeks; the main product is α -iodo- Δ^4 -butylene, $CHI\cdot CHEt$, a pale yellow liquid which decomposes gradually when exposed to light, b. p. 127 – 128° /atmospheric pressure, or 57° /30 mm. The same product is mainly obtained in a similar manner from the liquid $\alpha\beta$ -di-iodoethylene, but, in this case, an *isomeride* (probably the *cis*-modification), b. p. 168° , is produced in minor amount. It is converted by an excess of bromine in the presence of carbon tetrachloride into $\alpha\alpha\beta$ -tribromobutane, $CHBr_2\cdot CHBr\cdot CH_2\cdot CH_3$, a pale yellow liquid, b. p. 158° (partial decomp.)/normal pressure, or 98° /25 mm. The chief evidence with regard to the constitution of the iodobutylene rests on the observation

that it is converted by sodium into the hydrocarbon [Δ^8 -octadiene], C_8H_{14} , a colourless, slightly refractive liquid, b. p. 138–140°. The latter is transformed by ozone into the explosive *ozonide*, a yellowish-red, viscous liquid, which is decomposed by boiling water into glyoxal, propaldehyde, and hydrogen peroxide.

The transformation of the liquid (*cis*) $\alpha\beta$ -di-iodoethylene into the solid (*trans*-) modification has been observed repeatedly. The reverse change occurs to the extent of 45° in six hours, when the solid isomeride is heated carefully at 190°; slight decomposition with elimination of iodine occurs simultaneously. H. W.

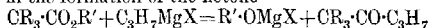
The System Water-Ethyl Alcohol-Chloroform: Miscibility of the Three Components in Different Proportions and some Practical Applications. N. SCHOORL and (Mlle) A. REGENBOGEN (*Rec. trav. chim.*, 1922, **41**, 1–14).—The ternary system has been examined and a diagram is given showing the limits of homogeneous mixtures at temperatures of 0°, 10°, 20°, and 66°. The results obtained by Bancroft (A., 1895, ii, 157) are criticised on the ground of incomplete drying of the alcohol used. The authors suggest that their data may be of use in the examination of spirits of wine for water content, and of chloroform for the detection of impurities. Details of some typical estimations carried out in this manner are given. H. J. E.

The System Ethyl Alcohol-Water-Aromatic Hydrocarbons from 30° to –30°. W. R. ORMANDY and E. C. CRAVEN (*J. Inst. Petroleum Tech.*, 1921, **7**, 422–439).—The freezing-point curves of binary mixtures of benzene with ethyl alcohol, toluene, and xylene, and of ternary mixtures of benzene, alcohol, and water, and of "benzole" (benzene 3, toluene 1), alcohol, and water were determined, and also the liquid separation points of ternary mixtures of benzene, toluene, and xylene with alcohol and water at temperatures ranging from –30° to +30°. The method adopted was to add from a burette dilute aqueous alcohol to known mixtures of absolute alcohol and the hydrocarbon, maintained at a constant temperature, until separation occurred. The full numerical results are given in numerous tables, and results obtained by graphical interpolation are also given showing the strengths of ethyl alcohol necessary to dissolve various proportions of benzene and toluene at 15° and xylene at 0°. For these, the original paper should be consulted. In regard to the binary mixtures of benzene and toluene, the depression of the freezing point of benzene follows the cryoscopic law over a considerable range. The results of the liquid separation point determinations on the ternary mixtures showed that at any temperature above the melting point of benzene the solubilities of the three hydrocarbons in an alcohol of given strength are in the order benzene-toluene-xylene. At temperatures below this, separation of solid phase occurs and the solubility of benzene falls below that of its homologues. G. F. M.

Some Properties of $\alpha\alpha$ -Disubstituted Esters. J. LEROIDE (*Ann. Chim.*, 1921, [ix], **16**, 354–410).— $\alpha\alpha$ -Disubstituted ketones react with magnesium alkyl haloids, in which the alkyl group has

a normal chain and not more than four carbon atoms, to give excellent yields of the corresponding secondary alcohols. Thus pinacolin reacts with magnesium propyl chloride to give $\beta\beta$ -dimethylbutan- γ -ol. Under similar conditions, camphenylone gives camphenylol. With magnesium propyl bromide, fenchone gives fenchyl alcohol and camphor gives a mixture of borneol and isoborneol.

The esters of $\alpha\alpha$ -disubstituted monobasic acids react with the same magnesium alkyl haloids to give principally secondary and not tertiary alcohols. This action is more marked with the magnesium alkyl iodides than with the bromides or chlorides. In all cases it is very slow, and the yields are by no means quantitative. This is probably due to the fact that the first part of the change consists in the formation of the ketone



which only takes place very slowly.

Ethyl pivalate reacts with magnesium ethyl iodide to give $\beta\beta$ -dimethylpentan- γ -ol, $\text{CMe}_3\cdot\text{CHEt}\cdot\text{OH}$, b. p. 140—148°, giving a phenylurethane, m. p. 83°; with magnesium propyl iodide, bromide, or chloride the products are $\beta\beta$ -dimethylhexan- γ -ol, $\text{CMe}_3\cdot\text{CHPr}\cdot\text{OH}$, b. p. 153—156°/755 mm.; n_D^{20} 1.4280; d_4^{20} 0.830, giving a phenylurethane, m. p. 68—69°; and $\beta\beta$ -dimethyl- γ -propylhexan- γ -ol, $\text{CMe}_3\cdot\text{CPr}_2\cdot\text{OH}$, b. p. 90°/20 mm.; n_D^{20} 1.4455; d_4^{20} 0.853. The ratio of the yield of secondary alcohol to that of the tertiary alcohol is greatest with magnesium propyl iodide and least with magnesium propyl chloride. On oxidation with chromic acid in acetic acid solution, $\beta\beta$ -dimethylhexan- γ -ol gives tert.-butyl propyl ketone, $\text{CMe}_3\cdot\text{COPr}$, b. p. 145—148°; n_D^{20} 1.4148; d_4^{20} 0.8225.

Ethyl pivalate reacts with magnesium butyl iodide to give $\beta\beta$ -dimethylheptan- γ -ol, $\text{CMe}_3\cdot\text{CH(OH)}\cdot\text{C}_4\text{H}_9$, b. p. 76—79°/16 mm., giving a phenylurethane, m. p. 65°.

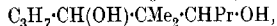
To examine the effect of heavier groups in the α -position in the disubstituted esters, ethyl α -methyl- α -propylvalerate has been prepared as follows and used. α -Propylvaleric acid yields with thionyl chloride the acid chloride, b. p. 77—79°/20 mm., which with benzene in the presence of aluminium chloride gives phenyl α -propylbutyl ketone, $\text{CHPr}_2\cdot\text{COPh}$, b. p. 157—159°/25 mm.; n_D^{20} 1.5064; d_4^{20} 0.9492 which with sodamide followed by methyl iodide gives some impure phenyl α -methyl- α -propylbutyl ketone. The latter ketone is better prepared by propylating propiophenone, which gives phenyl α -methylbutyl ketone, $\text{CHMePr}\cdot\text{COPh}$, b. p. 122—125°/14 mm.; n_D^{20} 1.5109; d_4^{20} 0.964, and this on further propylation yields phenyl α -methyl- α -propylbutyl ketone, $\text{CMePr}_2\cdot\text{COPh}$, b. p. 149—152°/13 mm.; n_D^{20} 1.5063; d_4^{20} 0.9502. The latter ketone on treatment with sodamide and subsequent hydrolysis with hydrochloric acid yields α -methyl- α -propylvaleric acid, $\text{CMePr}_2\cdot\text{CO}_2\text{H}$, m. p. 43—44°; b. p. 124—128°/18 mm., giving an amide and an ethyl ester, b. p. 90—92°/18 mm., which with magnesium propyl bromide yields δ -methyl- δ -propyloctan- ϵ -ol, $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CMePr}\cdot\text{CHPr}\cdot\text{OH}$, b. p. 109—112°/18 mm.; n_D^{20} 1.4421; d_4^{20} 0.8455; giving a phenylurethane, m. p. 96°, and its hydrate, m. p. 89—91°.

Ethyl campholate gives with magnesium propyl chloride or bromide 1 : 2 : 2 : 3-tetramethylcyclopentylpropylcarbinol,

$\text{CHMe} \cdot \text{CMe}_2 > \text{CMe} \cdot \text{CHPr} \cdot \text{OH}$, m. p. 58°; b. p. 126—129°/15 mm.

Using a straight chain ester of high molecular weight, namely, ethyl palmitate, a secondary alcohol was also obtained with magnesium propyl bromide, the product being *nonadecan-8-ol*, $\text{C}_{17}\text{H}_{35} \cdot \text{CHPr} \cdot \text{OH}$, m. p. 19°; b. p. 221—224°/15 mm., giving a *phenylurethane*, m. p. 50—51°.

The behaviour of the esters of $\alpha\alpha$ -disubstituted dibasic acids towards magnesium alkyl haloids is variable. Ethyl dimethylmalonate gives with magnesium propyl chloride a number of derivatives including a small amount of a bissecondary glycol, ethyl isobutyrate, dipropyl ketone, propyl isopropyl ketone, tripropylcarbinol, and dipropylcarbinol. There are thus apparently two reactions; one in which the molecule is split up giving tripropylcarbinol and the hydrocarbon resulting from its dehydration, and the other in which hydrogenation occurs. The new compounds isolated are: *$\alpha\alpha$ -dimethylnonan-8,9-diol*,



m. p. 73°; b. p. 150—152°/18 mm.; *tripropylcarbinol phenylurethane*, m. p. 74—75°; *dipropylisopropylcarbinol phenylurethane*, m. p. 71—72°. To confirm the formation of dipropyl and propyl isopropyl ketones, a similar condensation of magnesium isobutyl chloride and ethyl dimethylmalonate was carried out and from the products *diisobutyl ketone semicarbazone*, m. p. 119°, and *isopropyl isobutyl ketone semicarbazone*, m. p. 139—140°, were isolated. To prove the constitution of the nonandiol described above, the following preparations were made. Ethyl butyrate was condensed with methyl propyl ketone in the presence of sodium ethoxide to give *dibutylmethane*, $\text{C}_3\text{H}_7 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_3\text{H}_7$, b. p. 96—98°/21 mm.; n_D^{20} 1.46125; d_4^{20} 0.9218, giving a *copper derivative*, m. p. 157—158°. On methylation, it yielded *$\alpha\alpha$ -dibutylmethane*, $\text{CH}_3 \cdot \text{CH}(\text{COPr})_2$, b. p. 124—126°/21 mm., giving a *copper derivative*, m. p. 140—141°, and on further methylation *$\beta\beta$ -dibutylpropane*, $\text{CMe}_2(\text{COPr})_2$, b. p. 129—130°/18 mm., which gave a *disemicarbazone*, m. p. 216°, identical with that obtained from the nonandiol.

With a view to elucidating the course of the reaction of the dimethylmalonic ester and magnesium propyl chloride, dipropyl ketone was condensed with ethyl bromoisobutyrate in dry benzene in the presence of zinc, giving *ethyl 3-hydroxy- $\alpha\alpha$ -dimethyl- β -propylhexoate*, $\text{HO} \cdot \text{CPr}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$, b. p. 135—136°/26 mm., which, when treated with magnesium propyl bromide, has its molecule ruptured in such a way as to give tripropylcarbinol and a magnesium additive compound.

Ethyl $\alpha\alpha$ -dimethylsuccinate and magnesium propyl chloride yield 3 : 3-dimethyl-2 : 5 : 5-tripropyltetrahydrofuran, $\text{CH}_2 \cdot \text{CPr}_2 > \text{O}$, b. p. 114—118°/15 mm.; n_D^{20} 1.4531; d_4^{20} 0.8629.*

Ethyl $\alpha\alpha$ -dimethylglutarate and magnesium propyl bromide give

xx-dimethyl-δδ-dipropylvalerolactone, $\begin{matrix} \text{CH}_2\cdot\text{CMe}_2\cdot\text{CO} \\ | \\ \text{CH} \text{---} \text{CPr}_2 \end{matrix} > \text{O}$, b. p. 153—157/16 mm., n_D^{20} 1.4585, d_4^{20} 0.9311, giving a barium salt. Similarly, ethyl camphorate yields *dipropylcampholactone*, m. p. 58°; b. p. 177—180°/18 mm., giving a copper salt.

The presence of an alkyloxy-group in the ester results in the general reaction pursuing its normal course, giving a tertiary alcohol. Thus ethylethoxy-*x*-methylpropionate and magnesium propyl chloride give *β*-ethoxy-*β*-methyl-*γ*-propylhexan-*γ*-ol, $\text{OEt}\cdot\text{CMe}_2\cdot\text{CPr}_2\cdot\text{OH}$, b. p. 118—122°/35 mm.; n_D^{20} 1.4392; d_4^{20} 0.8864. Under similar conditions, ethyl *β*-hydroxy-*xxβ*-trimethylbutyrate gives *βγγ*-trimethyl-*δ*-propylheptan-*ββ*-diol, $\text{HO}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{CPr}_2\cdot\text{OH}$, m. p. 91°.

W. G.

Symmetrical Dichlorodimethyl Sulphide. IGNAZ BLOCH and FRITZ HÖHN (*Ber.*, 1922, **55**, [B], 53—57).—*Dichlorodimethyl sulphide* is prepared by cautious admixture of trithioformaldehyde and sulphur chloride and subsequent heating of the mixture under reflux after the initial violent action has subsided. It is an almost colourless liquid, b. p. 156—156.5°/765 mm., or 51°/11 mm. Its formation appears to take place in accordance with the equation: $(\text{CH}_2\text{S})_3 + 2\text{S}_2\text{Cl}_2 = \text{C}_2\text{H}_4\text{Cl}_2\text{S} + \text{CS}_2 + 2\text{HCl} + 4\text{S}$. It is converted by hot water into trithioformaldehyde and amorphous polyoxymethylene, and by methyl-alcoholic potassium hydroxide or ammonia solution into (?) polyoxymethylene and *s*-dimethoxydimethyl sulphide, b. p. 152°/760 mm. (cf. de Lattre, A., 1912, i, 745).

The formation of *s*-dichlorodimethyl sulphide from trithioformaldehyde brings additional confirmation of the constitution, $\text{S} < \begin{matrix} \text{CH}_2\cdot\text{S} \\ \text{CH}_2\cdot\text{S} \end{matrix} > \text{CH}_2$, generally assigned to this compound. H. W.

Production of Alcohols, Ketones, and the Like [Lithium Formate, Methyl Alcohol, Acetone, etc.]. BADISCHE ANILIN- & SODA-FABRIK (Brit. Pat. 173097).—Carbon monoxide may be utilised for the production of alcohols, ketones, etc., through the intermediate formation of lithium formate, which when heated at 380—420°, preferably in a current of moist hydrogen under diminished pressure, is decomposed with the formation of methyl alcohol, acetone, formaldehyde, etc., in addition to oily and empyreumatic substances. Lithium formate is obtained by the action of carbon monoxide on lithium hydroxide or carbonate in presence of water at a temperature of 120—250° and a pressure of 20—70 atm. When absorption is complete, the solution is evaporated and the dry salt powdered and transferred to the decomposition plant, which may consist of a tube-shaped vessel with a conveyor worm, or of shallow pans or revolving drums heated in a bath of fused potassium nitrate. The residue after decomposition, consisting of lithium carbonate and carbon, may be utilised again for the production of formate, but provision must be made, by washing the gases or otherwise, for the removal of the carbon dioxide pro-

duced during absorption of the monoxide: $\text{Li}_2\text{CO}_3 + \text{H}_2\text{O} + 2\text{CO} = 2\text{HCO}_2\text{Li} + \text{CO}_2$. G. F. M.

The Mode of Sudden Pyrogenic Decomposition of Acetic Acid at High Temperature. (Mlle) ÉGLANTINE PEYTRAL (*Bull. Soc. chim.*, 1922, [iv], **31**, 113—118; cf. A., 1918, i, 1; 1920, i, 217; 1921, i, 156, 166).—The sudden decomposition of acetic acid vapour at 1150° takes place in such a way that the molecule is deformed as little as possible. There are three reactions of the first order, namely, (1) $2\text{CH}_3\cdot\text{CO}_2\text{H} = (\text{CH}_3\cdot\text{CO})_2\text{O} + \text{H}_2\text{O}$; (2) $\text{CH}_3\cdot\text{CO}_2\text{H} = \text{CO}_2 + \text{CH}_3$; (3) $2\text{CH}_3\cdot\text{CO}_2\text{H} = 2\text{H}_2\text{O} + 2\text{CO} + \text{C}_2\text{H}_4$; and two reactions of the second order, namely, (4) $\text{CO}_2 + \text{CH}_3 = \text{CO} + \text{H}_2 + \text{H}_2\text{O} + \text{C}$; (5) $\text{C}_2\text{H}_4 = \text{C}_2\text{H}_2 + \text{H}_2$. The importance of reaction (1) is greater as the velocity of flow of the acetic acid vapour is greater. In reaction (4), instead of the formation of free carbon, very condensed hydrocarbons are probably formed. W. G.

The Mode of Pyrogenic Decomposition of Methyl Acetate at High Temperature. (Mlle) ÉGLANTINE PEYTRAL (*Bull. Soc. chim.*, 1922, [iv], **31**, 118—122; cf. preceding abstract).—In the pyrogenic decomposition of methyl acetate at high temperatures the two principal changes are:

- (1) $\text{CH}_3\cdot\text{CO}_2\text{Me} = \text{CH}_3\cdot\text{CHO} + \text{H}\cdot\text{CHO}$;
- (2) $2\text{CH}_3\cdot\text{CO}_2\text{Me} = 2\text{CH}_3\cdot\text{CO}_2\text{H} + \text{C}_2\text{H}_4$.

The acetaldehyde formed in reaction (1) tends to decompose, giving methane and carbon monoxide, and the formaldehyde gives hydrogen and carbon monoxide. The acetic acid formed in reaction (2), which is less important than reaction (1), tends to decompose in the manner already described (*loc. cit.*). W. G.

Carboxylic Esters as Amphoteric Electrolytes. H. V. EULER and OLOF SVANBERG (*Z. physiol. Chem.*, 1921, **115**, 139—146).—Ethyl acetate acts as an amphoteric electrolyte, the constant K_a being about 10^{-16} and K_b about 10^{-20} . S. S. Z.

Manufacture of Chloro-acids. KIKUNAE IKEDA and SHINTARO KODAMA (Jap. Pat. 37211).—By the action of sodium nitrite, solid or in concentrated solution, on amino-acid hydrochlorides or their ester hydrochlorides in the presence of hydrogen chloride, chloro-acids or their esters are easily produced. For example, 1 part of leucine or its hydrochloride is dissolved in 1—2 parts of the water layer obtained in the previous manufacture of the chloro-acid from leucine, and saturated with hydrogen chloride; the corresponding quantity of 30% sodium nitrite solution is gradually added at the ordinary temperature. Chlorohexioic acid separates as an oil. It is separated from the water layer, dried with sodium sulphate, and distilled in a vacuum. The method is applied to crude leucine, phenylalanine, valine, alanine, etc. CHEMICAL ABSTRACTS.

Reactions between the Higher Fatty Acids and Salts of the Lower Fatty Acids. ARTHUR W. KNAFF and RAYMOND V. WADSWORTH (*Chem. News*, 1922, **124**, 44—45).—If finely powdered sodium acetate is added to oils or melted fats, a gelatinous precipitate is

generally produced. Sodium propionate and sodium butyrate give similar results. Castor oil does not give a jelly. Pure glycerides do not give this reaction, which is due to the free fatty acids present. The jelly consists of soaps formed by the interaction of the salt and the free fatty acids. It is a reversible colloid. Sodium acetate is soluble in oleic acid, forming a viscous solution. When cooled this becomes a thick jelly. If the fatty acid is dissolved in absolute alcohol and the acetate added, a gelatinous precipitate of soap is formed almost immediately. The reaction is reversed by adding water.

H. C. R.

The Preparation of Acrylic Acid and some of its Derivatives.

J. H. N. VAN DER BURG (*Rec. trav. chim.*, 1922, **41**, 21—23; cf. Gaspary and Tollens, A., 1872, 814, and Moureu, A., 1893, i, 548).—The methods of preparation used hitherto are inconvenient when large quantities are required or give poor yields. The acid itself and some of its derivatives tend to polymerise on keeping and must therefore be freshly prepared. The sodium salt will keep in. definitely, and may be used as a starting-point. It is prepared from ethylene glycol, which gives a 70—80% yield of chlorohydrin. The latter is treated with sodium cyanide, the resulting nitrile being transformed into hydraacrylic acid. The sodium salt of the latter, carefully dried, gives, on distillation with sulphuric acid, very pure acrylic acid, and on treatment with phosphorus oxychloride, the chloride of the acid.

H. J. E.

Two New Ammonium Molybdomalates.

E. DARMOIS (*Compt. rend.*, 1922, **174**, 294—296; cf. A., 1920, ii, 575; 1921, i, 539).—From a study of the optical activity of solutions of different proportions of molybdic acid, malic acid, and ammonia, the existence of two levorotatory compounds having the compositions $\text{MoO}_3 \cdot 2\text{C}_4\text{H}_6\text{O}_5 \cdot 2\text{NH}_3$ and $\text{MoO}_3 \cdot 2\text{C}_4\text{H}_6\text{O}_5 \cdot 4\text{NH}_3$, respectively, has been proved and these two compounds and the corresponding sodium and potassium salts have been isolated.

W. G.

Equilibrium in Solution of the Desmotropic-Isomeric Diacetylsuccinic Esters and its Colorimetric Estimation.

L. KNORR and H. P. KAUFMANN (*Ber.*, 1922, **55**, [B], 232—248).—Ethyl diacetylsuccinate has been isolated in two diketonic forms, namely, β -ester, m. p. 89°, γ -ester (formerly α_3 -ester), m. p. 30°, one dienolic form, α -ester (formerly γ_4 -ester), and two keto-enolic forms, $\alpha\beta$ -ester (formerly γ_1 -ester), a liquid and $\alpha_2\beta$ -ester (formerly α_2 -ester), m. p. 20°. The equilibrium in solution in various solvents and the rate of transformation of the isomerides have been measured at 30° with the aid of the deeply-coloured enolic iron salts according to the method of Wislicenus (cf. also Knorr and Schubert, A., 1911, i, 948). In methyl and ethyl alcohols, acetone, and chloroform, the rate of enolisation of the β -ester at 30° diminishes with decreasing dielectric constant of the solvent; in hexane, ether, or benzene, the change takes place too slowly to permit its measurement. The influence of temperature on the velocity of transformation and the relative proportions in the equilibrium mixtures has

been examined, mainly by comparison of the data obtained at 30° and at the boiling points of the solutions. The velocity of enolisation is found to increase with increasing temperature, but the composition of the equilibrium mixture is approximately constant. In *N*/5, *N*/10, and *N*/20 solution, the concentration of the β -ester is without influence on the velocity of transformation or the composition of the equilibrium mixture. The influence of the dielectric constant of the solvent on the composition of the equilibrium mixture could not be elucidated definitely.

Examination of the equilibrium in hexane and ether led to the observation of an unexpectedly high enolic content, indicating the possible presence of the dienol, m. p. 45°. This is shown by mechanical separation of the products to be actually the case. The presence of this ester in molten mixtures or in dissolved equilibrium mixtures has not been established previously.

The iron salt of ethyl α -diacetylsuccinate is obtained when a solution of the β -ester in absolute alcohol is treated successively with an alcoholic solution of sodium ethoxide and an ethereal solution of ferric chloride; it is a brown powder. The analysed product, however, appears to be basic in character. The salt, $\text{FeCl}_2 \cdot \text{O} \cdot \text{CMe} \cdot \text{C}(\text{CO}_2\text{Et}) \cdot \text{C}(\text{CO}_2\text{Et}) \cdot \text{CMe} \cdot \text{O} \cdot \text{FeCl}_2$, a voluminous, unstable, violet-black powder, is prepared by agitating the brown salt with a solution of ferric chloride in anhydrous ether.

H. W.

New Method of Preparing Gluconic Acid. ARTHUR R. LING and DINSHAW RATTONJI NANJI (*J. Soc. Chem. Ind.*, 1922, 41, 28—29†; cf. Herzfeld and Lenart, A., 1920, i, 143).—A slow, well-regulated current of chlorine (about one bubble per second) is passed through a solution of dextrose (20%) containing 0.025% of cobalt nitrate as catalyst and a quantity of calcium bromide corresponding in potential bromine content with 26% of the bromine used by Herzfeld and Lenart (*loc. cit.*). The temperature is maintained at 45—50°, and care is taken that this limit is not exceeded, otherwise the hypobromous acid may be converted into bromate. As the reaction proceeds, there is a constant accumulation of halogen acids, and to avoid their retarding action calcium carbonate is added from time to time. The reaction is complete in about four hours. The final solution when reaction has proceeded normally contains calcium gluconate, calcium chloride, and calcium bromide, and when concentrated appropriately deposits the former in the course of a few days, the yield being about 90% of that theoretically possible.

The use of calcium bromide and chlorine is preferable to that of bromine, since the latter acts more efficiently in the nascent state, and there is no loss of bromine by volatilisation under the correct experimental conditions.

H. W.

Colophenic Acid. OSSIAN ASCHAN (*Ber.*, 1922, 55, [B], 1—3; cf. A., 1921, i, 512).—The author is unable to share Fahrion's view of the identity of colophenic acid with oxyabietic acid prepared by the autoxidation of colophony (A., 1907, i, 329; 1921, i, 792)

and points out that it is not possible for Fahrion's product to be homogeneous.

Colophenic acid is an excellent material for the preparation of varnishes.
H. W.

Sulphiformin (Methanalsulphurous Acid). PHILIPPE MALVEZIN (*Ind. chimique*, 1921, 8, 311–314; from *Chem. Zentr.*, 1921, iii, 1118).—Sulphiformin, obtained by the distillation of formaldehyde in the presence of sulphur dioxide, has the formula $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}\cdot\text{OH}$. It reduces Millon's reagent, and gives a violet coloration and precipitate with magenta solution. It decomposes readily, giving sulphur dioxide and formic acid. With aniline alone, a yellow dye is formed; in the presence of hydrochloric acid a red caoutchouc-like mass is formed; in the presence of acetic acid, a dye is obtained which is yellowish-green in the cold and orange-red on warming. Sulphiformin has antiseptic properties.
G. W. R.

Laboratory Preparation of Acetaldehyde. CHESTER E. ADAMS and ROGER J. WILLIAMS (*J. Amer. Chem. Soc.*, 1921, 43, 2420–2421).—In the preparation of acetaldehyde by the oxidation of ethyl alcohol with sodium dichromate the yield is practically doubled if the mixture is stirred vigorously to disengage the acetaldehyde as fast as it is formed. The best proportions to use are 200 grams of sodium dichromate for 100 grams of alcohol.
W. G.

Production of Butaldehyde and Butyric Acid therefrom. MATTHEW ATKINSON ADAM and DAVID ALLISTON LEGG (Brit. Pat. 173004).—Butaldehyde is obtained by the dehydrogenation of *n*-butyl alcohol by passing it in a state of vapour over a fused copper oxide catalyst heated at 280–320°, and fractionally distilling the product. About 75% conversion is obtainable by one passage over the catalyst at a good speed; for example, 240 c.c. per hour using a $\frac{3}{4}$ -inch copper tube packed for 26 inches of its length with the catalyst. Butyric acid is prepared from the liquid aldehyde by adding a small proportion of an oxygen-carrying catalyst, for example, manganese butyrate, and introducing air or oxygen at either ordinary or higher pressures, with suitable cooling to maintain the liquid below the boiling point of the aldehyde.
G. F. M.

The Mode of Pyrogenic Decomposition of Acetone at High Temperature. (Mlle) ÉGLANTINE PEYTRAL (*Bull. Soc. chim.*, 1922, [iv], 31, 122–124; cf. this vol., i, 219).—The sudden pyrogenic decomposition of acetone at high temperatures consists almost exclusively of a simple scission of the molecule into keten, CH_2CO , and methane. The keten then decomposes, giving carbon monoxide and ethylene.
W. G.

Monosulphates of Dextrose and Sucrose. III. CARL NEUBERG and LUDWIG LIEBERMANN (*Biochem. Z.*, 1921, 121, 326–332).—By the action of chlorosulphonic acid in pure chloroform

at -10° on a pyridine solution of dextrose or sucrose, the mono-sulphates of these carbohydrates are obtained and can be isolated as the calcium salts, which are amorphous. The calcium salt from sucrose sulphate has $[\alpha]_D +48.0$, that from dextrose sulphate $[\alpha]_D +44.43$. Lactose reacts similarly, but no details are given.

H. K.

The Action of Ozone on Pure Solutions of Dextrose, Lævulose, and Sucrose. C. W. SCHONEBAUM (*Rec. trav. chim.*, 1922, 41, 44—48).—Various workers in this field have obtained results which are mutually contradictory. The author finds that dextrose, lævulose, and sucrose in alkaline solution are decomposed quantitatively when ozonised, the products being carbon dioxide and water. Formic acid is obtained as an intermediate product. The reaction takes a considerable time, and, for this reason, various technical applications are suggested.

H. J. E.

New Observations on the Chemistry of the Sugars. II. H. KILIANI (*Ber.*, 1922, 55, [B], 75—101; cf. A., 1921, i, 304).—Further experience of the oxidation of sugars and polyhydroxy-acids by nitric acid at the atmospheric temperature has emphasised the necessity of excluding air during the process. This is effected conveniently by performing the operation in Erlenmeyer flasks provided with ground-glass stoppers and inserting at one point between the neck and the stopper a small plug of long-fibred glass wool. It is now recognised that the oxidation may lead to the production of α -keto-acids, the predominance of aldehydic or ketonic product appearing to depend on the configuration of the original material.

Attempts to replace the use of bromine and sodium hydroxide by that of a filtered solution of bleaching powder in the oxidation of the primary alcoholic to the aldehydic group in the sugars have not been quite satisfactory, possibly owing to deficient alkalinity of the solution.

Action of Nitric Acid on Dextrose and d-Gluconic Acid.—The product of the oxidation is, in all probability, α -ketogluconic acid, $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}(\text{OH})]_3\cdot\text{CO}\cdot\text{CO}_2\text{H}$; the acid is unstable when preserved at the atmospheric temperature, and evolves carbon dioxide when its aqueous solution is boiled. After successive addition of hydrocyanic acid and hydrolysis, a dibasic acid is produced which evolves carbon dioxide more freely than the parent acid; inability to effect the completion of the latter change has prevented its definite characterisation as a substituted malonic acid.

Preparation of Rhammonic Acid.—The acid is prepared more conveniently by the older bromine method than by the new oxidation process. It is emphasised that the oxidation of aldoses by bromine is never quantitative and that with freely soluble acids and lactones it is advisable to boil the solution of the acid (which has been freed from hydrobromic acid) with chalk for at least three-quarters of an hour; the solution is evaporated to small bulk and the calcium salt is precipitated with alcohol and

decomposed subsequently with oxalic acid. Contrary to the statements of the literature, pure rhamnolactone does not reduce alkaline copper solutions.

Action of Nitric Acid on Rhammonic Acid and Rhamnose.—The oxidation of either substance at the atmospheric temperature gives the lactone of α -ketorhammonic acid in good yield. The product has m. p. (indefinite) 188° (decomp.) after becoming discoloured at 168° , $[\alpha]_D -25.2^\circ$. The solubility in water is about 1 part in 20 parts at 20° . It gives a *p*-nitrophenylhydrazone, $C_{12}H_{13}O_6N_3.H_2O$, long, yellow needles, m. p. 150° after softening and darkening above 130° . It retains the terminal methyl group of rhammonic acid, since it is not oxidised by bromine water and yields acetic acid when treated with an aqueous suspension of silver oxide. The presence of the ketonic group in the α -position is deduced from the ability of the keto-lactone to evolve carbon dioxide from its boiling aqueous solution and the greater readiness with which the gas is evolved from the hydrolysed cyanohydrin of the keto-lactone.

Oxidation of α -Galaheptonic Acid by Nitric Acid.—*l*-Mannohepturonic lactone (from *d*-galactose), m. p. $205-206^\circ$ (decomp.) after becoming discoloured at about 190° , is obtained in good yield from α -galaheptonic acid; the aldehydic nature of the product has been established.

Configuration of Digitoxone and Digitoxosecarboxylic Acid.—Digitoxone, $CH_3[CH(OH)]_5.CH_2.CHO$, is oxidised by nitric acid to a dihydroxyglutaric acid and meso-tartaric acid, thus showing that the hydroxyl groups, 3 and 4, are in the meso-position to one another. Since the lactone of digitoxonic acid has been shown previously to be levorotatory, the annexed configuration can be assigned to digitoxonic acid on the basis of Hudson's rule. On the other hand, the proof of the meso-position of the 3- and 4-hydroxyl groups of digitoxonic acid can now be extended. The well-crystallised lactone of digitoxosecarboxylic acid is levorotatory ($[\alpha]_D -13.67^\circ$), as is also the phenylhydrazone of digitoxosecarboxylic acid (groups of needles, m. p. $145-148^\circ$, $[\alpha]_D -37.7^\circ$). In consequence, the newly-formed hydroxyl group in the production of cyanohydrin must be to the left and digitoxosecarboxylic acid receives the annexed configuration, in which the configuration of the 6-CH-OH remains unelucidated.

Formation of Digitalonic Acid from Digitalose (cf. A., 1916, i, 493).—Digitalonic acid gives a well-crystallised, levorotatory lactone, and must therefore contain a hydroxyl group attached to carbon atom 4. The methoxyl group cannot be in position 5, since the acid does not give pure trihydroxyglutaric acid when oxidised by nitric acid. It must therefore have the latter group in position 3 or 2. The former possibility is discounted by the apparent inability of digitalose to yield an osazone. Since the phenylhydrazone of digitalonic acid is levorotatory ($[\alpha]_D$ about -16°)

the configuration $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}\cdot\overset{\text{OMe}}{\underset{\text{H}}{\text{C}}}\cdot\text{CO}_2\text{H}$ may be assigned to the parent acid.

Salts of Trihydroxyadipic Acid (from Metasaccharin).—The following salts are described, generally with particular reference to their solubility in water: calcium, *strontium* (+4H₂O), *magnesium* (+3H₂O), barium, *potassium*, C₆H₈O₇·K₂·H₂O, silver, *cadmium* (+2H₂O), *quinine*. The behaviour of the calcium and quinine salts of *l*-trihydroxyglutaric acid is described in detail. The cadmium, barium, and calcium salts of α -galaheptanepentol-dicarboxylic acid have been further investigated.

The crystallisation of *d*-galactonic acid is readily effected by evaporation of solutions of the acid (from the calcium salt and oxalic acid) in an open dish and subsequent treatment of the paste obtained in this manner with alcohol under conditions which are specified in detail in the original.

The preparation of the galaheptonic acid from *d*-galactone is described in detail, the process depending on a modification of Fischer's phenylhydrazide method.

The production of *l*-mannonic and *l*-gluconic acids from arabinose has been investigated further. Under conditions which are fully described, the cyanohydrin synthesis leads to the crystallisation of *l*-mannonamide, which is smoothly converted into *l*-mannonic acid by boiling barium hydroxide solution. The isolation of *l*-gluconic acid from the mother-liquors is conveniently effected by means of the brucine salt.

H. W.

The Partial Replacement of the Acid Groups in β -Penta-acetylglucose. PERCY BRIGL (*Z. physiol. Chem.*, 1921, **116**, 1–52).—The following compounds have been prepared:

α -Chloro- $\gamma\epsilon\zeta$ -triacetyl- β -trichloroacetylglucose from β -penta-acetylglucose and phosphorus pentachloride, forms long, white needles, m. p. 142°, $[\alpha]_D^{20} +2.95^\circ$ in benzene. The position of the chlorine atoms was ascertained by various forms of saponification. $\beta\gamma\epsilon\zeta$ -Tetracetyl- α -trichloroacetylglucose from β -penta-acetylglucose, trichloroacetyl chloride, and phosphorus oxychloride, forms dense needles, m. p. 131°, $[\alpha]_D^{20} +94.6^\circ$. $\alpha\gamma\epsilon\zeta$ -Tetracetyl- β -trichloroacetylglucose, by treating the tetrachloro-substance with anhydrous zinc chloride and acetic anhydride. A mixture of two isomerides obtained has m. p. 110–112°. The α -isomeride forms long, fine needles, m. p. 120°, $[\alpha]_D^{20} +101.5^\circ$; the β -isomeride forms needles, m. p. 167°, $[\alpha]_D^{20} +28.85^\circ$. α -Chloro- $\gamma\epsilon\zeta$ -triacetyl- β -monochloroacetylglucose, by reduction of tetrachlorine compound, needles, m. p. 81°. α -Chloro- $\gamma\epsilon\zeta$ -triacetylglucose, from the tetrachloro-compound with an ethereal solution of ammonia, crystallises in needles, m. p. 158°; it exhibits multirotation, the initial $[\alpha]_D^{20} +25.0^\circ$ rising to $+151.5^\circ$. α -Chloro- $\gamma\epsilon\zeta$ -triacetylglucose- β -chlorosulphinite, $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}<\overset{\text{CH}(\text{OAc})}{\underset{\text{O}}{\text{C}}}\cdot\overset{\text{CH}(\text{OAc})}{\underset{\text{CHCl}}{\text{C}}}\cdot\text{SOCl}$, by treating the last compound with thionyl chloride, has m. p. 103° (approx.).

$\alpha\beta$ -Dichloro- $\gamma\zeta$ -triacetylglucose, from triacetylchloroglucose with phosphorus pentachloride, crystallises in platelets, m. p. 83° , $[\alpha]_D^{25} + 65.6^\circ$. Triacetylglucal from triacetyldichloroglucose, by treatment with zinc dust. Acetobromoglucose was also converted into acetochloroglucose with mercuric chloride. S. S. Z.

The Synthesis of Disaccharides containing Sulphur and Selenium by combining two Dextrose Residues in the C β position. Some New Derivatives of ζ -Bromoglucose. FREIZ WREDE (*Z. physiol. Chem.*, 1921, **115**, 284–304).—The following compounds have been prepared: Acetodibromoglucose from penta-acetyl glucose, $[\alpha]_D^{25} + 184.1^\circ$ in ethyl acetate. Methylglucoside- ζ -bromohydrin triacetate, $[\alpha]_D^{25} - 7.78^\circ$ in ethyl acetate, from the last compound. Triacetyl-ethylglucoside- ζ -bromohydrin from acetodibromoglucose and ethyl alcohol in the presence of dry silver carbonate, crystallises from methyl alcohol in compact needles, m. p. 154° (uncorr.): $[\alpha]_D^{25} - 11.78^\circ$ in ethyl acetate. β -Tetra-acetyl- ζ -bromoglucose, by heating acetodibromoglucose with acetic anhydride and sodium acetate at 100° , melts at 127° (corr.). The α -form, produced at the same time, crystallises from methyl alcohol in fine, white needles, m. p. 171° , $[\alpha]_D^{25} + 107.2^\circ$ in ethyl acetate. Dimethylglucoside of bisglucosyl ζ -sulphide hexa-acetate, from triacetylmethylglucoside- ζ -bromohydrin and alcoholic potassium sulphide by heating in a sealed tube, crystallises in white needles, m. p. 168° , $[\alpha]_D^{25} - 10.51^\circ$ in ethyl acetate. Dimethylglucoside of bisglucosyl ζ -sulphide, from the hexa-acetate by treating it with absolute methyl alcohol and ammonia in the cold, crystallises in dense masses, m. p. 188° , $[\alpha]_D^{25} + 6.53^\circ$ in water. Bisglucosyl ζ -sulphide, by heating the last compound with 5% sulphuric acid in a sealed tube, sinters at approximately 135° and liquefies at approximately 150° , $[\alpha]_D^{25} + 80.9^\circ$ in water. Octa-acetyl-bisglucosyl ζ -sulphide, by acetylating the last compound, crystallises in nodules, m. p. 163° , $[\alpha]_D^{25} + 56.2^\circ$ in ethyl acetate. Dimethylglucoside of bisglucosyl ζ -selenide hexa-acetate, prepared in the same way as the sulphide, crystallises in long, white needles, m. p. 179 – 180° . Dimethylglucoside of bisglucosyl ζ -selenide, prepared in the same way as the sulphide, crystallises from 90% alcohol in dense aggregates, m. p. 138° , $[\alpha]_D^{25} + 14.59^\circ$ in water. Bisglucosyl ζ -selenide, by hydrolysis from the glucoside, sinters at approximately 160° , decomposes at approximately 200° , $[\alpha]_D^{25} + 69.5^\circ$ in water. Octa-acetyl-bisglucosyl ζ -selenide, by acetylating the selenide with acetic anhydride, crystallises from ether and light petroleum in nodules, m. p. 150 – 155° , $\alpha_D + 40^\circ$ (approx.). Dimethylglucoside of bisglucosyl ζ -diselenide hexa-acetate, by treatment of acetyl-methylglucoside- ζ -bromohydrin with an alcoholic solution of potassium diselenide, has m. p. 148° , $[\alpha]_D^{25} + 49.74^\circ$ in ethyl acetate. Dimethylglucoside of bisglucosyl ζ -diselenide, by treatment with methyl alcohol solution and gaseous ammonia, crystallises from 98% alcohol in dense needles, m. p. 96 – 97° , $[\alpha]_D^{25} + 75.65^\circ$ in water. Bisglucosyl ζ -diselenide, by hydrolysis of the methyl glucoside, decomposes at

approximately 125° , $[\alpha]_D^{25} +145.6^\circ$ in water. *Octa-acetyl-bis-glucosyl ζ -diselenide*, by acetylation of the last compound with acetic anhydride, forms small crystals which sintered at $175-179^\circ$.
S. S. Z.

Unsaturated Reduction Products of the Sugars and their Transformations. III. 2-Deoxyglucose (Glucodesose). MAX BERGMANN, HERBERT SCHOTTE, and WOLFGANG LECHINSKY (*Ber.*, 1922, **55**, [B], 158—172; cf. *A.*, 1921, i, 307, 648).—With the object of obtaining a derivative of dextrose so modified that a hydroxyl group is not present in position 2, glucal (*A.*, 1913, i, 445; 1914, i, 252; 1920, i, 420) has been converted by dilute acid into 2-deoxyglucose, $\text{OH}\cdot\text{CH}\cdot\text{CH}_2\cdot\underset{\text{O}}{\underset{|}{\text{CH}}}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, which

has only been isolated previously in the form of its phenylbenzylhydrazone. In connexion with this substance, it is proposed to define a simple sugar as an aldehyde-alcohol or keto-alcohol with an open carbon chain and one or more hydroxyl groups, of which at least one is in the direct neighbourhood of the carbonyl radicle; deoxyglucose and Kiliani's digitoxose are therefore not within the class. It is also proposed to establish a nomenclature for the 2-deoxy-sugars by inserting the syllable "des" between the name of the sugar from which they are derived and the characteristic ending of all sugars "ose"; thus 2-deoxyglucose is termed "glucodesose."

2-Deoxyglucose is prepared by hydrolysing triacetylglucal by means of methyl-alcoholic ammonia to glucal and treatment of the latter with 2*N*-sulphuric acid at 0° . Alternatively, triacetylglucal is treated directly with 2*N*-sulphuric acid at $10-15^\circ$ and the deoxyglucose is converted into its phenylbenzylhydrazone, m. p. $158-159^\circ$, from which it is regenerated by treatment with benzaldehyde containing 10% of benzoic acid. The first method is preferred. 2-Deoxyglucose is a white, anhydrous powder, m. p. 148° (corr.), to a turbid liquid which decomposes at about 155° , $[\alpha]_D^{25} +46.59^\circ$ in water, $+17.56^\circ$ in pyridine. It does not appear to be mutarotatory in aqueous solution, although it has been isolated in two forms with differing specific rotation (details will be given later). It behaves in the same manner as dextrose towards Fehling's solution, alkaline silver solution, and magenta-sulphurous acid. It gives a yellow coloration with warm alkali hydroxides. It is very readily decomposed by not too dilute acid, with separation of greyish-green or darker amorphous substances; the reaction may be used for the detection of deoxyglucose and for distinguishing it from the true sugars. A pine shaving dipped into a solution of deoxyglucose and then exposed to hydrogen chloride becomes intensely green (these reactions are also shown by Kiliani's digitoxose). *Deoxyglucosyl phenylmethylhydrazone* crystallises in colourless needles or prisms, m. p. $157-158^\circ$ (corr.), decomp. about 195° ; the corresponding *p*-nitrophenylhydrazone forms small, canary-yellow prisms, m. p. $190-191^\circ$ (corr., decomp.). Deoxyglucose could not be fermented by a number of varieties of yeast.

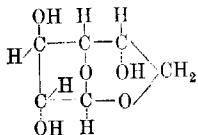
Deoxyglucose is distinguished by the extreme ease with which it is converted into glucosido-derivatives by acids in the presence of alcohols. Small amounts of acetic acid cause the production of glucoside in a short time at 100° , whilst with methyl alcohol containing 0.25–1% of hydrogen chloride the formation of the methylglucoside is complete in less than fifteen minutes at the atmospheric temperature. The product has m. p. $91\text{--}92^{\circ}$ after softening at 87° , $[\alpha]_D^{20} +137.8^{\circ}$ in aqueous solution, whereas the isomeride described previously has m. p. $122\text{--}123^{\circ}$, $[\alpha]_D -48.2^{\circ}$. The difference in the specific rotation (186°) is approximately the same as that between α - and β -methylglucosides (189°). Since in all probability the two methyldeoxyglucosides are similarly related to one another and contain the oxygen bridge between the 1 and 4 carbon atoms, it is proposed to designate the first-named substance α -2-deoxymethylglucoside [α -methylglucoside] and the latter β -2-deoxymethylglucoside. The sensitiveness of the two substances towards acidic hydrolysing agents is similar, and closely resembles that of γ -methylglucoside. Fission of the glucoside appears to be facilitated by the absence of the hydroxyl group from position 2. α -2-Deoxymethylglucoside, like the β -isomeride, is not affected by yeast or emulsin.

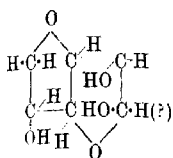
Glucosose tetrabenzoate is prepared by the action of benzoyl chloride on glucosose in the presence of pyridine and chloroform; it crystallises in rectangular plates or short, broad prisms. The preparation, m. p. $136\text{--}145^{\circ}$, appears to be a mixture of isomerides.

H. W.

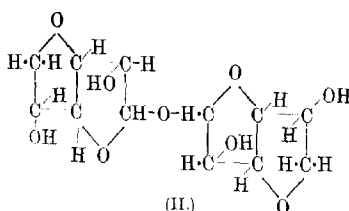
The Constitution and Configuration of the Anhydro-sugars.

P. KARRER and ALEX. P. SMIRNOV (*Helv. Chim. Acta*, 1922, 5, 124–128).—Triacetyl-lævoglucosan is converted by liquid hydrogen bromide at the atmospheric temperature in the course of a few days into acetodibromoglucose (A., 1912, i, 239), thus confirming the constitution assigned to lævoglucosan by Pictet (A., 1920, i, 819). The reaction is effected more advantageously by the use of phosphorus pentabromide, and, in this form, is the readiest and best method of preparing acetodibromoglucose. Assuming that a displacement of the oxygen bridge and of an acetyl residue does not occur during the change (which is very improbable by reason of the relative stability of lævoglucosan and the non-convertibility of penta-acetylglucose into acetodibromoglucose by means of phosphorus pentabromide), the annexed configuration can be assigned to lævoglucosan. Anhydroglucose has the configuration 1, in which the disposition of the hydrogen and hydroxyl attached to the α -carbon atom is undecided. The formula accounts for the unusual stability of the compound, since it is composed of two five-membered rings and shows further that anhydro-compounds are only to be expected from sugars which have the γ - and δ -hydroxy-groups on opposite sides of the carbon chain.



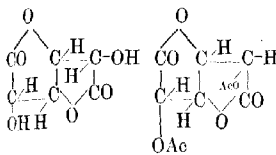


(I.)

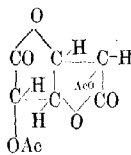


(II.)

Diglucan and isodiglucan (A., 1921, i, 765) are represented by formula II, in which the configuration at the α -carbon atoms remains undetermined.



(III.)



(IV.)

therefore represented by the formulae III and IV.

H. W.

Polysaccharides. XIII. Inulin and the Alkali Hydroxide Compounds of the Anhydro-sugars.

P. KARRER, MAX STAUB, and A. WÄLTI (*Helv. Chim. Acta*, 1922, 5, 129—139; cf. this vol., i, 11).—It has been shown previously (A., 1921, i, 765) that polymeric anhydro-sugars form additive compounds with sodium hydroxide of the type $(C_{12}H_{20}O_{10}, NaOH)_x$, which are dissociated more or less readily by water. It is now shown that these compounds can be prepared conveniently by precipitating them from their solutions in sodium hydroxide (8—10%) by alcohol and washing the precipitates thoroughly with alcohol (96%). The use of absolute alcohol does not generally effect the complete removal of absorbed sodium hydroxide. The compounds of α -diamylose, α -tetra-amylose, β -hexa-amylose, and α -octa-amylose with potassium hydroxide have been prepared in a similar manner and conform to the type $(C_{12}H_{20}O_{10}, KOH)_x$. *Inulin sodium hydroxide*, $(C_6H_{10}O_5, NaOH)_x$, is prepared by dissolving inulin in sodium hydroxide solution (8%) and adding the product to a large volume of alcohol, and is purified by re-solution in a little water and re-precipitation by alcohol. *Inulin potassium hydroxide*, $(C_6H_{10}O_5, KOH)_x$, is more readily dissociated than the corresponding sodium compound, and is prepared from solution containing 15% or more of potassium hydroxide. The isolation of these compounds brings additional evidence in favour of the view that inulin is a polymeric form of anhydro-fructose. Further confirmation is found in the behaviour of inulin towards fission with acetyl bromide under conditions which cause only slight disintegration of disaccharides such as maltose; the only compound obtained was fructose, although the action was carried out at 0° to +5°, and for only such time as was necessary to effect the solution of the inulin.

H. W.

Speed of Reaction in Concentrated Solutions and the Mechanism of the Inversion of Sucrose. GEORGE SCATCHARD (*J. Amer. Chem. Soc.*, 1921, 43, 2387—2406).—A theoretical paper in which a method is outlined for calculating the activity of water in sucrose solutions of any concentration at temperatures near the ordinary temperature. The method is also extended to solutions containing a small amount of another solute, such as sulphuric acid. A formula for the speed of the reaction in solution in terms of the activities of the reacting substances is developed, and it is suggested as the most logical formula for solutions. By the application of this formula to the inversion of sucrose, it is shown that the available data indicate that the reaction is of the sixth order with respect to water. The results are interpreted as indicating the existence of a hexahydrate of sucrose. The effect of the addition of sucrose in increasing the activity of the hydrogen ion is explained as being very largely due to an increase in the molar fraction of hydrogen ions without any large change in the actual degree of ionisation. Precautions, necessary in calculating the catalytic effect of the non-ionised portion of the acid by the customary method, are pointed out. J. F. S.

Hydration of Sucrose in Water Solution as Calculated from Vapour Pressure Measurements. GEORGE SCATCHARD (*J. Amer. Chem. Soc.*, 1921, 43, 2406—2418; cf. preceding abstract).—The average degree of hydration of sucrose in water solution at 0° and 30° is calculated from the vapour pressures of sucrose solutions. The hypothesis is advanced that sucrose solutions are equilibrium mixtures of water, unhydrated sucrose, and a single hydrate of sucrose, and that the relative quantities of these substances are determined by the law of mass action. This hypothesis is tested by comparison of the experimental results with those calculated from the law of mass action. The agreement is fair for either a hexahydrate or a heptahydrate. The hypothesis is further tested by a comparison of the activity of the sucrose calculated from its degree of hydration and that calculated by the Duhem-Margules equation. The results confirm those obtained by the use of the law of mass action method. The present results are in keeping with those obtained from the inversion of sucrose (*loc. cit.*). J. F. S.

Preservation of Starch Solution. NAOTSUNA KANÔ (*J. Chem. Soc. Japan*, 1921, 42, 974—975).—Starch solution (50 c.c.) for use as an indicator in iodometry can be preserved for more than eight months by the addition of 0.5 c.c. of 2N-hydrochloric acid, or of a drop of carbon disulphide. K. K.

The Constitution of Polysaccharides. J. J. LYNST ZWIKKER (*Rec. trav. chim.*, 1922, 41, 49—53).—On the assumption that the polysaccharide molecule may be regarded as formed from a small number of hexose molecules, each of which consists of a straight chain of carbon atoms, the author shows that a regular tetrahedron and a triangular prism, each bounded by such a straight chain

lying along the junction of each pair of sides, gives a structural formula which is in accordance with the properties of cellulose and starch respectively. Such a structure involves the homogeneous filling of space, and is consistent with the opinion that the polysaccharide molecule is not built up of long chains of sugar molecules.

H. J. E.

The Composition of Agar. M. SAMEC and V. SSAJEVIĆ (*Compt. rend.*, 1921, 173, 1474—1475).—Evidence is given in support of the view that agar is a sulphuric ester of gelose in much the same way as amylopectin is a phosphoric ester of the amyloses. A gram-atom of sulphur in the gelose ester corresponds with 9320 grams of organic matter. The great viscosity of agar is probably due to its relatively high content of the SO_4'' ion.

W. G.

Alkali-cellulose and the Structure of Cellulose. P. KARRER (*Cellulosechemie*, 1921, 2, 125—128).—The experimental results of Gladstone are confirmed, namely, that the product of the action of strong sodium hydroxide solution on cellulose, after complete washing with alcohol, has a constant composition corresponding with the formula $\text{C}_{12}\text{H}_{20}\text{O}_{10}\cdot\text{NaOH}$. This is regarded as a definite additive compound, which is hydrolysed by water, so that the products obtained with dilute sodium hydroxide are the results of equilibria. Alkali-cellulose therefore falls into line with analogous compounds obtained with starch, inulin, and the various polymerides of anhydro-maltose classed as amyloses. All these combine with sodium hydroxide in the same proportions, regardless of the degree of polymerisation. Cellulose is a polymeride of cellobiose anhydride, and it is probable from analogies based on the heats of combustion and the Röntgen spectrum (cf. A., 1921, i, 310, 397, 771) that the degree of polymerisation is not high. It is suggested that the cellulose formula may be written $(\text{C}_{12}\text{H}_{20}\text{O}_{10})_2$ and that the polymerisation of the anhydro-sugar takes place through subsidiary valencies without the rupture of the oxygen bridges. The cellulose fibre-substance has a configuration analogous to a crystal structure with nuclei of these dimeride molecules in co-ordinated arrangements. The molecules are held together in the crystal by other valency forces of unusual strength, and this strong cohesion accounts for the properties hitherto attributed to a highly polymerised molecule. The tendency is for the cellulose matter to concentrate its mass into the smallest possible volume and to assume a co-ordinated arrangement of its molecules.

J. F. B.

A New Degradation of Cellulose ; Conversion of Cellulose into a Biose Anhydride. P. KARRER (*Ber.*, 1922, 55, [B], 153—156).—A reply to the criticisms of Hess (this vol., i, 12). The conversion of amylose by acetyl bromide into acetyl-bromomaltose is "quantitative" in the sense that the same yield of this substance is obtained from maltose, amylose, or starch. The process of the depolymerisation of starch does not appear to be involved in this matter.

H. W.

Saccharification of Cellulose. A. WOHL and H. KRULL (*Cellulosechemie*, 1921, 2, 1—7).—When cellulose is moistened with 3 parts of water, cooled with ice, saturated with hydrogen chloride, kept for five hours at 20°, the acid removed by evaporation in a vacuum at temperatures up to 70°, the residue dissolved in water to form a 10% solution containing 1% of hydrogen chloride and boiled for eight hours, 97% of the theoretical quantity of reducing sugars is obtained and can be estimated by cupric reduction. The process may be applied to the estimation of cellulose. In view of discrepancies in the yields of alcohol obtained by fermentation of the reducing sugars from pine wood and from pure cellulose respectively, it is probable that the hydrolysis of the cellulose in the former is impeded by incrusting substances which cannot be removed by preliminary treatment, whilst prolonged action of the acid leads to the formation of non-fermentable reversion products in relatively large quantity.

CHEMICAL ABSTRACTS.

Viscosity of some Cellulose Acetate Solutions. GUY BARR and L. L. BIRCUMSHAW (*Trans. Faraday Soc.*, 1921, 16, Appendix, 72—75).—The viscosity and density of 5% solutions of cellulose acetate have been determined in acetone and mixtures of acetone and water, benzene, and ethyl alcohol respectively. The second solvent was added in all concentrations up to the point where cellulose acetate was precipitated. The viscosity-concentration (of second solvent) curves are markedly different. Benzene causes a progressive increase in the viscosity with increase in the concentration, whereas water and ethyl alcohol give an initial rapid fall in viscosity, which in the case of water reaches a minimum and then rises fairly rapidly but with alcohol remains fairly constant at the minimum value.

J. F. S.

Syntheses with Chloroacetyl Chloride. W. LEIGH BARNETT (*J. Soc. Chem. Ind.*, 1921, 40, 286; cf. A., 1921, i, 847).—Examination of the gases evolved during the reaction between chloroacetyl chloride and cellulose showed that hydrogen chloride alone is formed in the absence of water, but on treating the acetic acid solution of the cellulose esters with water, large quantities of formic acid are produced. The author concludes that the reaction proceeds in four distinct stages, and has succeeded in preparing compounds corresponding with all these stages in the case of glycerol.

W. P. S.

The Elimination of Furfuraldehyde from Oxycelluloses. The Solubility in Alkali and the Reduction Capacity of Oxycelluloses. CARL G. SCHWALBE and ERNST BECKER (*Zellstoff u. Papier*, 1921, 1, 100—103; 135—139).—The yield of furfuraldehyde on treatment with barium hydroxide is not a characteristic property of oxycelluloses, and there are marked differences in their copper number, acidity, and resistance to alkali. The values obtained indicate the existence of two classes of oxycelluloses, in which the predominating character is acidic and aldehydic respectively, whilst the former character is almost completely lacking

in the hydrocelluloses. Denitrated wood pulp and denitrated nitro-silk (Chardonnnet silk) have the chemical character of the oxycelluloses and the hydrocelluloses respectively.

CHEMICAL ABSTRACTS.

Physico-chemical Characterisation of Lignin from Winter Rye Straw. ERNST BECKMANN, OTTO LIESCHE, and FRITZ LEHMANN (*Biochem. Z.*, 1921, **121**, 293—310; cf. *A.*, 1921, i, 546).—The formula $C_{40}H_{44}O_{15}$ for lignin has been confirmed in a number of ways. There are four methoxyl groups present and on benzoylation four benzoyl groups enter the molecule. The sodium salt of lignin contains slightly less than two sodium atoms. The molecular weight in phenol and in boiling acetic acid and that of the sodium salt in water agrees with the above formula. Conductivity measurements show that lignin obeys the Ostwald valency rule. H. K.

The Lignin-like Resins and Tannins of Spruce Needles. A. CLEVE VON EULER (*Cellulosechemie*, 1921, **2**, 128—135; 1922, **3**, 1—7; cf. *A.*, 1921, i, 769, 849; 1922, i, 100).—Powdered spruce needles were exhaustively extracted with 93% commercial methyl alcohol and the concentrated extract was divided into three fractions by means of ether. There were thus obtained: "crude fat," soluble in ether, "molasses," the brown, aqueous bottom layer, and "crude resin," an intermediate layer soluble in alcohol but not in ether. The crude fat contained, besides true resins and fats, about 29% of humus-like substances classified under the name of abiophyllic acids, consisting of allied derivatives of coniferyl aldehyde more or less condensed and partly hydrogenised. The crude resin, which amounted to not less than 10% of the weight of the needles, might be described as a hydrated form, partly hydrogenised, of lignin; that is to say, it is an allied substance, at a lower stage of condensation than the ordinary lignin of wood. Its composition, C=60.6, H=7.12%, has no relation to that of a true resin; it is, moreover, extremely susceptible to change, either spontaneously or by solution in alkali and reprecipitation by acid, giving a brownish-red product not unlike the phlobaphens derived from tannic acid. The alcoholic solution of the crude resin has the property of precipitating gelatin. A study of the constituents of the "molasses" soluble in water yielded a whole series of definitely pronounced tannins which have been fractionated and classified into components soluble and insoluble in ethyl acetate, some yielding uncoloured lead salts and others lemon-yellow lead salts. A comparison of this series of needle tannins with the series of bark tannins studied by Etti and Böttinger (*Ber.*, **22**, 753; **23**, 647) revealed many analogies. The spruce-needle tannins are ketonic acids, most of them hydroaromatic, related to *p*-cumarylferulic acid or ferulylferulic acid at various degrees of hydrogenation; derivatives related to caffeic acid are also represented. Those giving colourless lead salts and insoluble in ethyl acetate are richest in hydrogen and those giving yellow lead salts are poorest. According to Klason's hypothesis (*A.*, 1920, i, 821), β -lignin is a ketonic acid, not hydroaromatic, but otherwise very closely related

to this series of water-soluble spruce-needle tannins. The author formulates β -lignin as a dihydroxyhydrocaffeoylferulic acid. All these tannins and β -lignin are built up from more or less hydrogenised hydroxycinnamic acids. The author does not accept Klason's flavone constitution for α -lignin; he regards it as being very similar to β -lignin, but built up from more or less hydrogenised hydroxycinnamic acids and aldehydes; the abiephylic acids are built up of similar aldehydes, and the tannins of the crude resin of similar aldehydes and alcohols. The following formula might represent α -lignin, except that it includes two hydroxyls, instead of one as determined by Klason,

$\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_2(\text{OH})(\text{OMe})\cdot\text{CH}\cdot\text{CH}\cdot\text{CHO}$,
and the tannins of the crude resin and abiephylic acids would be derived from this by various additions of H_2O and H_2 . J. F. B.

Preparation of Amines from Alcohols and Ammonia.

EUGENIE SMOLENSKI and KAZIMIR SMOLENSKI (*Roczniki Chemji*, 1921, 1, 232—243).—When the vapours of methyl, ethyl, or amyl alcohol react with ammonia in the presence of a dehydrating catalyst such as alumina or kaolin at about 300° , a satisfactory yield of primary, secondary, and tertiary amines is obtained. In the case of ethyl alcohol, secondary products consisting of ethylene and ethyl ether are also obtained. If the ratio of the quantities of alcohol to ammonia is about 2 mols : 1 mol, when the temperature is kept between 300° and 330° , a good yield of diethylamine is obtained. The total yield, after accounting for the alcohol which is regained, is 53% of amine, 25% of ether, and 20% of ethylene. Under the same conditions, ethyl ether and ammonia also give ethylamine. Good results are obtained with aromatic compounds; thus aniline and methyl alcohol at 350° in the proportion of 1 mol. : 4 mols. give toluidines and xyldines, but if the temperature is kept below 330° and 10—20% of a salt of aniline is added, the yield of the homologues of aniline is practically zero. J. F. S.

Action of some Acyclic Halogenated Derivatives on Hexamethylenetetramine. MARCEL DELÉPINE and (MME) PIERRE JAFFEUX (*Bull. Soc. chim.*, 1922, [iv], 31, 108—112).—With the exception of isopropyl iodide, secondary and tertiary alkyl haloids do not form quaternary ammonium salts with hexamethylenetetramine. Primary alkyl haloids do, but the ease of the action diminishes as the molecular weight increases. Alkyl haloids having the same molecular weight but differing in the branching of the chain differ in their reactivity. W. G.

Condensation Products from Acid Haloids. IX. Ketenium Compounds. E. WEDEKIND and CL. WEINAND (*Ber.*, 1922, 55, [B], 60—68; cf. Wedekind and Miller, A., 1909, i, 459).—It has been shown previously that isobutyryl chloride and phenylchloroacetyl chloride are converted by triethylamine into dimethylketentriethylum, $\text{CMe}_2\cdot\text{CO}\cdot\text{NEt}_3$, and phenylchloroketentriethylum, $\text{CPhCl}\cdot\text{CO}\cdot\text{NEt}_3$. The similar reactions with chloroacetyl chloride, bromoacetyl chloride, and dichloroacetyl chloride are now described. For this

type of compound the constitutions $\text{NEt}_3 \left\langle \begin{smallmatrix} \text{CR}_2 \\ \text{CO} \end{smallmatrix} \right.$ and $\text{NEt}_3 \left\langle \begin{smallmatrix} \text{O} \\ \text{C}:\text{CR}_2 \end{smallmatrix} \right.$ have been advanced tentatively. The first of these, however, is excluded by the observation that dimethylketentriethylum is smoothly hydrogenated in the presence of platinum black to isobutaldehyde and triethylamine: $\text{NEt}_3 \left\langle \begin{smallmatrix} \text{O} \\ \text{C}:\text{CMe}_2 \end{smallmatrix} \right. \rightarrow$

$(\text{NEt}_3 \left\langle \begin{smallmatrix} \text{O} \\ \text{CH}:\text{CMe}_2 \end{smallmatrix} \right.)) \rightarrow \text{CHMe}_2\text{CHO} + \text{NEt}_3$. The incapability of existence of the assumed intermediate compound, combined with the improbability of the direct addition of a saturated tertiary amine at a C=O group, cause the authors to prefer the subsidiary valency formula, $\text{CR}_2\text{C}:\text{O} \dots \text{NAlk}_3$. An explanation is thereby afforded of the inability of the pre-formed keten to combine with triethylamine, since it is probable that in it the subsidiary valencies have to some extent compensated one another.

[With M. MILLER.]—Solutions of the requisite acid chloride and triethylamine are gradually mixed, when a violent reaction occurs; the product is filtered and the residue extracted with benzene, whereby triethylamine hydrochloride remains undissolved. The ketenium compound is isolated by distillation of the residue left after removal of the solvent from the filtrate under diminished pressure. The yields are small.

Chloroketentriethylum, $\text{CHClCO}\cdot\text{NEt}_3$, is an almost colourless liquid, b. p. $120\text{--}125^\circ/10$ mm. *Bromoketentriethylum*, a pale yellow liquid, b. p. $128\text{--}129.5^\circ/18$ mm., is transformed by hydrochloric acid at 135° into triethylamine hydrochloride and bromoacetic acid. It cannot be hydrogenated in the presence of palladium, towards which it behaves as a poison. *Dichloroketentriethylum* is a golden-yellow liquid, b. p. $142\text{--}145^\circ/18$ mm. It is decomposed by alcoholic potassium hydroxide solution with quantitative production of potassium chloride; carbon monoxide is not, however, evolved. H. W.

The Action of Amino-acids on Sugars. L. GRÜNHUT and J. WEBER (*Biochem. Z.*, 1921, **121**, 109—119).—The interaction between various amino-acids and sugars with special reference to melanoidin formation has been followed by a study of the formol titration, the optical activity, and reducing power. The reaction is in general very complex, and varies from case to case. H. K.

Alkylation of the Anhydrides of Amino-acids. P. KARRER, CH. GRÄNACHER, and A. SCHLOSSER (*Helv. Chim. Acta*, 1922, **5**, 139—141; cf. Sasaki and Hashimoto, this vol., i, 56).—Sarcosine anhydride is obtained in more than 50% yield by the protracted action of methyl iodide on the silver salt of glycine anhydride. An attempt to prepare the silver salt of leucine anhydride by the method used for the corresponding glycine compound was unsuccessful.

In general, very marked differences are found in the behaviour of the anhydrides of various amino-acids for which, at present, a

satisfactory explanation cannot be given. Thus, for example, glycine anhydride and phenylalanine anhydride give sparingly soluble additive compounds with solutions of calcium chloride in alcohol, but this behaviour is not exhibited by leucine anhydride.

H. W.

Monochlorocarbamide. Preparation of Chlorohydrins by its Action on Ethylenic Hydrocarbons. ANDRÉ DETEUF (*Bull. Soc. chim.*, 1922, [iv], **31**, 102—108).—Monochlorocarbamide may be obtained by the action of chlorine on carbamide in the presence of a small amount of water at 0°. By this method a certain amount of carbamide hydrochloride is also formed. The chlorocarbamide may be obtained in approximately 20% solution by passing chlorine through a solution of 120 grams of carbamide in 60 grams of water at 0°, in which 60 grams of powdered marble is suspended, until the theoretical amount of chlorine is taken up. The solution is then filtered. Such a solution, after the addition of 5% of acetic acid, readily reacts with ethylenic hydrocarbons, giving the corresponding chlorohydrins. For the latter action to take place, the solution of chlorocarbamide must be acid either from the addition of acetic acid or from the presence of carbamide hydrochloride.

W. G.

Preparation of Thiocarbamides. THE GOODYEAR TIRE AND RUBBER CO. (Brit. Pat. 164326).—In the preparation of substituted thiocarbamides by the action of carbon disulphide on a primary amine, the speed of the reaction is greatly increased and a product of greater purity is obtained if the reaction is carried out at a temperature above the boiling point of carbon disulphide, but below that of the amine, by passing, for example, the superheated vapours of carbon disulphide into the amine previously heated to the desired temperature.

G. F. M.

Isomeric Citraconyl Hydrazides. FREDERICK DANIEL CHATTAWAY and DERIC WILLIAM PARKES (*T.*, 1922, **121**, 283—288).

Simultaneous Reduction and Oxidation. III. Transformation of Halogenaldehydes into Aldehydes and Acids through Ketenes. ARTHUR KÖTZ and H. RATHERT (*J. pr. Chem.*, 1921, [ii], **103**, 227—240; cf. *A.*, 1913, i, 1309; 1915, i, 208).— $\beta\beta$ -Dichloro- α -acetoxyacrylonitrile when hydrolysed with strong sulphuric acid in the cold, gives $\beta\beta$ -dichloro- α -acetoxyacrylamide, $\text{CCl}_2\text{C}(\text{OAc})\cdot\text{CO}\cdot\text{NH}_2$, needles, m. p. 122—123°. The nitrile on boiling with water gives dichloroacetic acid, acetic acid, and hydrogen cyanide, and when heated with ethyl alcohol at 150°, it gives dichloroacetic acid, acetic ester, and hydrogen cyanide. It also reacts readily with aniline to give the corresponding anilides and hydrogen cyanide, and not dichloroketen. Ethyl β -dichloro- α -ethoxyacrylate, on the other hand, gives on boiling with water dichloroacetaldehyde, alcohol, and carbon dioxide. Dichloroacetoxyacrylonitrile, on reduction with hydrogen in presence of colloidal palladium or platinum black, gives $\beta\beta$ -dichloro- α -acetoxy propionitrile, $\text{CHCl}_2\text{CH}(\text{OAc})\text{CN}$, b. p. 42—43°/6 mm., and with

dry hydrogen chloride it gives $\alpha\beta$ -trichloro- α -acetoxypropionitrile, $\text{CHCl}_2\cdot\text{CCl}(\text{OAc})\cdot\text{CN}$, b. p. 202° , which on hydrolysis gives dichloroacetic acid, hydrogen chloride, and hydrogen cyanide, thus proving its structure. Dichloroacetoxyacrylonitrile, with alcoholic hydrogen chloride, gives the hydrochloride of the iminoether of $\alpha\beta$ -trichloro- α -acetoxyacetic acid, $\text{CCl}_2\text{H}\cdot\text{CCl}(\text{OAc})\cdot\text{C}(\text{OEt})\cdot\text{NH}_2\cdot\text{HCl}$, m. p. 93 – 94° . Bromoacetaldehyde, when heated in a sealed tube with triethylamine, gives diketocyclobutane, b. p. 125 – 126° . Chloral does not, under similar conditions, eliminate hydrogen chloride and give dichloroketen. W. Ö. K.

Aliphatic Diazo-compounds. XXIV. Organic Phosphorus Compounds. VI. Preparation and Reactions of Phosphazines.

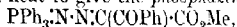
H. STAUDINGER and G. LÜSCHER (*Helv. Chim. Acta*, 1922, 5, 75–86).—A continuation of the work of Staudinger and Meyer (A., 1920, i, 105). The aliphatic diazo-compounds do not exhibit great differences in the readiness with which they combine with tertiary phosphines to give phosphazines. The latter are hydrolysed with greater or less readiness by water into hydrazones and phosphine oxides. They all decompose with evolution of nitrogen when heated, but the formation of phosphinemethylenes thereby is not observed except in the case of triphenylphosphine-benzophenoneazine (*loc. cit.*). Clear proof is adduced that the initial change consists of a dissociation of the compound into its constituents, since volatile diazo-compounds can be distilled unchanged from the difficultly volatile triphenylphosphine when the compounds are heated carefully in a vacuum.

Triphenylphosphinebenzilazine, $\text{PPh}_3\cdot\text{N}\cdot\text{N}\cdot\text{CPhBz}$, a yellow, crystalline powder, m. p. 115 – 117° (decomp.), is obtained in 83% yield by mixing benzoylphenyldiazomethane and triphenylphosphine in ethereal solution. It is hydrolysed readily by alcohol (90%) to triphenylphosphine oxide and benzilhydrazone. It is decomposed by heat in a complicated manner, giving nitrogen, triphenylphosphine, triphenylphosphine oxide, possibly benzonitrile, and a dark brown resin.

Ethyl triphenylphosphineglyoxylate-azine [from triphenylphosphine and ethyl diazoacetate (cf. Staudinger and Meyer, *loc. cit.*)] is hydrolysed with great readiness to triphenylphosphine oxide and ethyl anti-glyoxylatehydrazone, m. p. 38° , thus indicating the anti-configuration, $\text{CO}_2\text{Et}\cdot\overset{\text{H}}{\underset{\text{N}\cdot\text{N}\cdot\text{PPh}_3}{\text{C}}}$, for the phosphazine. It

decomposes at 200° with liberation of about half the total quantity of nitrogen; when distilled at 140° in a vacuum, it yields ethyl diazoacetate and triphenylphosphine.

Triphenylphosphine and methyl benzoyldiazoacetate react without development of heat to give the phosphazine,



a pale yellow, crystalline powder, m. p. 132.5 – 133° (decomp.). It is converted by alcohol (90%) into the substance, $\text{C}_{28}\text{H}_{25}\text{O}_4\text{N}_2\text{P}$, m. p. 95.5 – 96.5° . It gives nitrogen, triphenylphosphine, triphenylphosphine oxide, and resinous matter when heated.

Triphenylphosphine and methyl cinnamoyldiazoacetate yield the *phosphazine*, $\text{PPh}_3\text{:N:N:C(CO}_2\text{Me):CO-CH:CHPh}$, a pale yellow solid, m. p. 174° .

Ethyl triphenylphosphineacetylglyoxylate-azine,
 $\text{PPh}_3\text{:N:N:CAc:CO}_2\text{Et}$,

yellow crystals, m. p. 90° , is hydrolysed readily by atmospheric moisture. It decomposes completely when heated under atmospheric pressure; it regenerates its components when heated in a vacuum.

Triphenylphosphine and ethyl diazomalonate react comparatively slowly to give the *phosphazine*, $\text{PPh}_3\text{:N:N:C(CO}_2\text{Et)}_2$, almost colourless crystals, m. p. 128° (decomp.). It is very sensitive towards moisture and is hydrolysed readily to ethyl mesoxalatehydrazone and triphenylphosphine oxide. Towards heat, it behaves in the same manner as the preceding compound. The corresponding *phosphazine*, $\text{PPh}_3\text{:N:N:C(CO}_2\text{Me)}_2$, a pale yellow, crystalline mass, m. p. about 92° , crystallises more readily than the ethyl compound, but, like the latter, is extremely sensitive to moisture. It dissociates into its components when heated in an absolute vacuum.

Triphenylphosphine and benzoylacetyldiazomethane give the *phosphazine*, $\text{PPh}_3\text{:N:N:CAcBz}$, dark yellow crystals, m. p. 128° , which is hydrolysed by boiling dilute alcohol with the formation of *benzoylacetylketonehydrazone*, $\text{NH}_2\text{:N:CAcBz}$, colourless crystals, m. p. $111\text{--}112^\circ$; it decomposes completely when heated.

Triphenylphosphinedinitroquinoneazine (annexed formula), brilliant, red crystals, decomp. about 194° , is prepared from its components in chloroform solution. Relatively, it is an extremely stable substance, possibly owing to its sparing solubility; protracted heating with aqueous alcohol converts it into triphenylphosphine oxide and smeary products.

Further investigation of the decomposition of triphenylphosphinefluorenoneazine by heat has shown that the main product is the ketazine, m. p. 264° ; triphenylphosphinediphenylenemethylene, m. p. 274° , is produced in minor amount, but the method is unsuitable for its preparation for this reason, and also because of the difficulty of separating it from the ketazine by crystallisation.

H. W.

Aliphatic Diazo-compounds. XXV. Ketens. XXXVIII.
Aliphatic Diazo-compounds and Ketens. H. STAUDINGER
(Helv. Chim. Acta, 1922, 5, 87--103).—A theoretical paper. Further investigation has led the author to modify his view of the constitution of the aliphatic diazo-compounds (*A.*, 1916, i, 847), which are now formulated in accordance with the manner proposed by Angeli and Thiele. Compounds with the group :N:N: , which are derived from the unsaturated nitrogen molecule, are termed azens. This class of compound shows a great variety of chemical actions, some of which are common to all members of the class, whereas others are limited to particular members. The observations may be explained by the assumption that the azens contain two re-

active points, as indicated by the schemes $\text{A}:\text{N}:\text{N} <$ and $\text{A}:\text{N}:\text{N}$, respectively. Reactions occurring at the terminal nitrogen atom (first scheme), such as the addition of phosphines, reduction of aliphatic diazo-compounds and azides and addition of Grignard's reagents, are common to all azens, since an alteration in the nature or substitution of the first atom has relatively little influence on the third atom. Great differences in the reactivity of the different azens are observed, on the other hand, in many reactions which are considered to be based on compounds formulated in accordance with the second scheme; instances are afforded by (1) the addition of unsaturated compounds which is presumed to occur thus, $\text{R}_2\text{C}=\text{N}=\text{N} + \text{A}=\text{B} \rightarrow \text{R}_2\text{C}=\text{N}=\text{N} \xrightarrow{\text{A}=\text{B}} \text{R}_2\text{C} < \begin{smallmatrix} \text{A} \\ \text{B} \end{smallmatrix}$; (2) the action of compounds HR (acids, water, alcohols, and amines) proceeding according to the scheme $\text{R}_2\text{C}=\text{N}=\text{N} + \text{HCl} \rightarrow \text{R}_2\text{C}=\text{N}=\text{NH} \xrightarrow{\text{Cl}} \text{R}_2\text{CHCl} + \text{N}_2$; (3) the addition of halogen, acid chloride, or nitrogen dioxide. Reduction may occur in accordance with either scheme, the course of the changes being dependent on the particular azen and the reducing agent employed. A number of reactions cannot be explained by either scheme; in all of these the azens react with salts.

Carbonylen compounds resemble the azens closely in their general reactions, which may be referred to the two schemes $\text{R}_2\text{C}=\text{C}=\text{O}$, $\text{R} \cdot \text{N}=\text{C}=\text{O}$ or $\text{R}_2\text{C}=\text{C}=\text{O} <$, $\text{R} \cdot \text{N}=\text{C}=\text{O} <$ and $\text{R}_2\text{C}=\text{C}=\text{O}$, $\text{R} \cdot \text{N}=\text{C}=\text{O}$. Those occurring in accordance with the first scheme are but little affected by substituents at the third atom, and are exemplified by the action with phosphineimines, $\text{CH}_2=\text{C}=\text{O} + \text{PR}_3=\text{NPh} \rightarrow \text{CH}_2\text{C}(\text{NPh})\text{PR}_3$, the addition of tertiary phosphines, $\text{CPh}_2=\text{C}=\text{O} < + \text{PEt}_3 \rightarrow \text{CPh}_2=\text{C}=\text{O}=\text{PEt}_3$, and the action of compounds of the type HR, such as water, alcohol, acids, and primary and secondary amines. Reactions occurring in accordance with the second scheme are affected greatly by the presence of substituents at atom 3; typical instances are afforded by the behaviour towards oxygen and unsaturated compounds such as ethylene derivatives, Schiff's bases, carbonyl compounds, thioketones, and nitroso-compounds, by the polymerisation of ketens and by the decomposition of carbonylens by heat.

The similarity of azens and carbonylens extends to colour and to absorption spectrum. Further consideration of unsaturated substances leads to the recognition of the existence of two distinct groups, which are influenced differently by substituents, frequently in a reversed direction; one class includes the ketens and diazo-compounds, whereas the other comprises the carbonyl compounds and their nitrogenous derivatives, such as the hydrazones, Schiff's bases, ketazines, and phosphazines. These differences are most readily explained in accordance with Thiele's theory of partial valencies. In the cases of the highly reactive *o*-diketones and

unsaturated ketones, there is a strengthened partial valency at the end of the conjugated system $O=C-C=O$, which accounts for both the increase in the colour and enhanced activity. In the less reactive carbonyl substituted ketens and carbonyl substituted and unsaturated diazo-compounds, conjugation influences the second atom, which has but little effect on the reactivity, whereas the third atom is weakened in its action by the neutralisation of the partial valencies, thus $O=C-C=C=O$ and $O=C-C=N=N$ instead of $R_2C=C=O$ and $R_2C=N=N$, respectively. H. W.

Ketens. XXXIX. Aliphatic Diazo-compounds. XXVI. Behaviour of Ring Systems. H. STAUDINGER (*Helv. Chim. Acta*, 1922, 5, 103-108).—A general review of the stability of cyclic compounds formed from carbonylens and azens and unsaturated substances.

The four-membered rings, obtained in large number from diphenylketen and unsaturated compounds, are shown in tabular form; a general conception of the dependence of stability of these structures on the members of the ring cannot be given, but the effect of substituents is very marked. Five-membered rings are formed from azens and unsaturated compounds, which, in general, are exceedingly unstable and immediately lose nitrogen, with the production of three-membered rings. The five-atom rings containing one double bond are less stable than similar rings with two double bonds. Heterocyclic rings containing three atoms are less stable than the trimethylene derivatives; the influence of substituents is very marked, and requires further investigation.

H. W.

A New Process for the Preparation of Cadmium Dimethyl. E. DE MAHLER (*Bull. Soc. chim.*, 1922, [iv], 31, 125).—Cadmium iodide and magnesium methyl iodide readily react in ethereal solution at the ordinary temperature, giving cadmium dimethyl and magnesium iodide. The cadmium dimethyl, b. p. $105^\circ/760$ mm., is readily separated by fractional distillation.

W. G.

Stereoisomerism of Cyclic Hydrocarbons. A. SKITA and A. SCHENCK (*Ber.*, 1922, 55, [B], 144-152).—If Auwer's hypothesis (A., 1920, i, 721) that the reduction of aromatic hydrocarbons by Sabatier's method and in the presence of platinum leads to the formation of *trans*- and *cis*-derivatives respectively is correct, it must be possible to prepare a large number of previously unknown cyclic hexamethylenes by the latter process. For this purpose, a modification of the catalyst is, however, necessary, since the addition of water, which is necessary for the solution of the catalyst protected by gum arabic, causes the separation of the hydrocarbon. A glacial acetic acid reversible platinum colloid in which the metal is deposited on pure gelatin has therefore been introduced (the details of the preparation will be described later), with which it is possible to secure the smooth reduction of benzenoid hydrocarbons to hexamethylenes.

Reduction of the three xylenes is effected by dissolving the hydrocarbon in glacial acetic acid and adding successively solutions of chloroplatinic acid and gelatin in glacial acetic acid and colloidal platinum solution; hydrogenation is completed rapidly at 80° under an excess pressure of three atmospheres. In each case a mixture is obtained which is separated by repeated fractional distillation into its components, the purity of which is controlled by observation of the molecular coefficient of refraction. The following constants are recorded: 1^c:2^c-dimethylcyclohexane, b. p. 126.5°, d_4^{20} 0.786, n_D^{20} 1.43114; 1^c:2^t-dimethylcyclohexane, b. p. 124°, d_4^{20} 0.780, n_D^{20} 1.43037; 1^c:3^c-dimethylcyclohexane, b. p. 121.5°, d_4^{20} 0.775, n_D^{20} 1.42609; 1^c:3^t-dimethylcyclohexane, b. p. 119°, d_4^{20} 0.772, n_D^{20} 1.42470; 1^c:4^c-dimethylcyclohexane, b. p. 121.5°, d_4^{20} 0.773, n_D^{20} 1.42300; 1^c:4^t-dimethylcyclohexane, b. p. 119.5°, d_4^{20} 0.769, n_D^{20} 1.42095. The constants of the *trans*-series are identical with those of the products obtained by von Auwers by Sabatier's method. *p*-Cymene is reduced exclusively to 1^c-methyl-4^c-isopropylcyclohexane, b. p. 168.5°, d_4^{20} 0.816, n_D^{20} 1.45149. 1^c:2^c:4^c-Tetramethylcyclohexane, b. p. 146°, d_4^{20} 0.790, n_D^{20} 1.43314, is obtained a sole product of the reduction of ψ -cumenene by the new process; it is identical with the substance obtained recently (A., 1919, i, 578) by the catalytic reduction of ψ -cumenol in acid solution, and differs markedly from the 1^c:2^c:4^c-isomeride obtained by von Auwers by Sabatier's method. The 1^c:2^c:4^c-isomeride, b. p. 140°, d_4^{20} 0.774, n_D^{20} 1.42916 is prepared by the reduction of tetrahydro- ψ -cumenene (from *cis*-1-hydroxy-*cis*-2:4:5-trimethylcyclohexane) with sodium and alcohol.

The differences observed with the cyclohexenes are similar to those with the saturated cyclic hydrocarbons. Thus the 1:2:4-trimethylcyclohexene derived from *cis*-1-hydroxy-*cis*-2:4:5-trimethylcyclohexane in contrast to the stereoisomeric hydrocarbon obtained by von Auwers (*loc. cit.*) by Sabatier's method has a pronounced *cis*-form, the constants being b. p. 147°, d_4^{20} 0.814, n_D^{20} 1.44905 for the former and b. p. 145°, d_4^{20} 0.805, n_D^{20} 1.44820 for the latter.

cis-1-Hydroxy-*cis*-2:4:5-trimethylcyclohexane is converted into the corresponding ketone, which is converted by magnesium methyl iodide into the tertiary alcohol; the latter is transformed by phosphorus pentachloride into a tetrahydrodurene, b. p. 169°, d_4^{20} 0.828, n_D^{20} 1.46053. In all probability it is the 1^c:2^c:4:5-compound, whereas the isomeride, b. p. 166°, d_4^{20} 0.817, n_D^{20} 1.45722, obtained by von Auwers by Sabatier's method, has the 1^c:2^t:4:5-configuration. H. W.

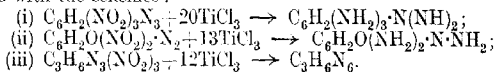
Action of Sodium Sulphite on Nitrobenzene. SEYEWETZ and VIGNAT (*Compt. rend.*, 1922, 174, 296—299).—When nitrobenzene in suspension is boiled with a 10—20% solution of sodium sulphite, it gradually disappears, the solution becoming orange-coloured and ammonia being evolved. From the solution, a compound can be isolated which is apparently identical with 4-aminophenol-3-sulphonic acid (cf. Schultz and Ståble, A., 1904,

i, 597). Phenylhydroxylaminesulphonic acid is probably formed as an intermediate product, and, being unstable, is transformed into the aminophenolsulphonic acid. The coloration is probably due to the formation of an azoxybenzene, and may be suppressed by adding sodium hydrogen carbonate to the sulphite solution.

W. G.

The Products of Nitration of Toluene. WILLIAM HOWESON GIBSON, REBECCA DUCKHAM, and RUTH FAIRBAIRN (T., 1922, 121, 270—283).

Reductions with Titanium Trichloride. HANS RATHSBURG (*Ber.*, 1921, 54, [B], 3183—3184).—The following nitro-compounds are completely reduced by titanium trichloride according to the method of Knecht and Hibbert in boiling, concentrated hydrochloric acid solution in a current of carbon dioxide: *s*-chloro-trinitrobenzene, trinitroresorcinol, trinitrophenylhydroxylamine, picramide, *m*-dinitro-*o*-dinitrosobenzene, picramic acid, tetranitrophenol (+4H₂O), trinitrophloroglucinol (+½H₂O). Over-reduction is observed with hexanitrotetrahydroxydiphenyl. If account is taken of the partial reduction of other groups which are present in addition to the nitro-radicles, trinitrophenyldiazomide, dinitrodiazophenol anhydride, and the substance, C₆H₆O₆N₆, from hexamethylenetetramine can be reduced smoothly in accordance with the schemes:



Complete reduction occurs also with the following salts and salt-like compounds, a disturbing influence due to the metallic ion not being observed: lead styphnate (+1H₂O), lead picrate, and the potassium compounds of dinitrodinitrosobenzene (+0.25H₂O) and tetranitrophenol (+1H₂O).

H. W.

The Electrochemical Oxidation of *o*-Toluenesulphonamide. FR. FICHTER and HANS LÖWE (*Helv. Chim. Acta*, 1922, 5, 60—69).—An examination of the possibility of converting *o*-toluenesulphonamide into "saccharin" by electrochemical oxidation.

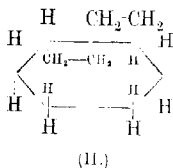
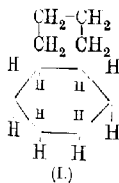
Electrolysis of solutions of *o*-toluenesulphonamide in an excess of aqueous sodium hydroxide at platinum, nickel, or copper anodes (cf. D.R.-P. 85491) does not lead to the formation of more than slight traces of "saccharin"; the sulphonamide appears to be completely decomposed with the formation of sodium sulphate as the sole isolable product.

Electrolysis of *o*-toluenesulphonamide, partly suspended and partly dissolved in 0.5*N*-sulphuric acid, at 60° with anodes of platinum gauze, graphite, or lead coated with lead peroxide in a divided cell in which the cathode is formed of a lead cylinder immersed in 2*N*-sulphuric acid causes the separation of ammonia, which is not due to hydrolysis and the production of small quantities of "saccharin." It is thus shown to be possible to oxidise the

methyl to the carboxy-group. For the successful production of "saccharin," however, it is necessary to secure the smooth oxidation of the methyl radicle and to protect the sulphonamide group during the process so as to secure the ultimate formation of the sulphonimide ring. The first point is investigated by examining the oxidation of *o*-toluenesulphonic acid in 0.5*N*-sulphuric acid solution at a rotating anode of lead covered with lead peroxide. It is found that the substance is not transformed smoothly into *o*-sulphobenzoic acid. A portion of it is oxidised to phenolic substances which still contain the sulphonic group; according to analyses of the barium salts, the phenolic substances and the products which are not precipitable with lead acetate are sulphocarboxylic acids. The electrolytic oxidation of *o*-toluenesulphonic acid proceeds therefore beyond the *o*-sulphobenzoic acid stage, and, for the preparation of "saccharin," it is necessary to protect the oxidised product by ring closure immediately the methyl is converted into carboxyl. Electrolysis of benzenesulphonamide, *o*-toluenesulphonamide, and "saccharin" in 0.5*N*-sulphuric acid solution at a platinum gauze anode proves that neither the sulphonamide nor the sulphonimide group is stable under these conditions. These groups, however, can be considerably protected by the use of ammoniacal solutions in which the ammonia functions as "relative depolariser"; thus, *o*-toluenesulphonamide is converted in 4*N*-ammoniacal solution in the presence of ammonium sulphate at 40° and at a platinum gauze anode into "saccharin," the material yield being 43.7% and the current yield 9.2%. The most favourable results, however (material yield 75.4%, current yield 42.6%), are obtained by the electrolysis of *o*-toluenesulphonamide dissolved and suspended in 2*N*-sodium carbonate solution at about 60° with a platinum gauze anode and rotating lead cathode, which secures efficient agitation of the mixture; a porous cell is unnecessary. The success of the method does not depend on the intermediate formation of potassium percarbonate.

H. W.

Theory of the *cis-trans*-Isomerism of Decahydronaphthalene. ERNST MOHR (*Ber.*, 1922, 55, [B], 230—231).—Willstätter and Waldschmidt-Leitz, in a recent discussion of the



theoretically possible number of isomerides in completely hydrogenated naphthalene derivatives, have expressed the opinion that only the *cis*-form (I) is capable of existence (*A.*, 1921, i, 667). Since, however, the author has been able to construct a model for both *cis*- and *trans*-tetrahydronaphthalene (II) which is completely free from strain (*cf.* *A.*, 1919, ii, 229), he considers that the ultimate experimental realisation of the *trans*-isomeride is possible.

H. W.

Certain Chloronaphthalene Derivatives. P. FRIEDLÄNDER, S. KARAMESSINIS, and O. SCHENK (*Ber.*, 1922, 55, [B], 45—52).—The chlorination of nitronaphthalenesulphonic acids leads to the elimination of the sulphonic group which is replaced by chlorine. The reaction is not quite quantitative, since, even with the calculated quantity of the reagents, a certain amount of oxidation occurs, leading apparently to the production of chloroquinones, which, however, are readily separated from the chloronitronaphthalenes by means of alkali.

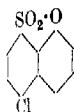
Gradual addition of an aqueous solution of sodium chlorate at 90—95° to a solution of sodium 1-nitronaphthalene-5-sulphonate in aqueous hydrochloric acid yields 5-chloro-1-nitronaphthalene, almost colourless needles, m. p. 111°; it is preferable to remove the chloronitronaphthalene from the mixture as it is formed by means of di-(tri-)chlorobenzene. 5-Chloro- α -naphthylamine crystallises in long, colourless needles, m. p. 85°, whilst its *acetyl* derivative forms hexagonal prisms, m. p. 128°. The crude chloronitronaphthalene contains small amounts of 1:4:5-trichloronaphthalene, m. p. 133°. 1-Nitronaphthalene-8-sulphonic acid is transformed similarly into 8-chloro-1-nitronaphthalene.

2-Nitronaphthalene-4:8-disulphonic acid is the main product of the nitration of naphthalene-1:5-disulphonic acid (the *sodium* salt, lustrous needles, and the sparingly soluble *barium* salt, $C_{10}H_6O_8NS_2Ba$, are described); it is converted by chlorination into 4:8-dichloro-2-nitronaphthalene, long, yellow needles, m. p. 132°. The latter is reduced by stannous chloride or iron and hydrochloric acid to 4:8-dichloro- β -naphthylamine, colourless needles, m. p. 132—133° (the *hydrochloride*, and the *acetyl* derivative, colourless needles, m. p. 265°, are described). The base can be diazotised in concentrated sulphuric acid solution, from which the *diazonium sulphate* is precipitated by addition of water in small, pale yellow needles. The latter couples normally with phenols and naphthols; it is transformed by boiling dilute sulphuric acid into 4:8-dichloro- β -naphthol, colourless needles, m. p. 158—159° (*methyl ether*, needles, m. p. 93°), and by hydrochloric acid and cuprous chloride into 2:4:8-trichloronaphthalene, yellow needles, m. p. 94°.

4:8-Dichloro-1-nitronaphthalene, pale yellow needles, m. p. 142°, is prepared by the chlorination of 1-nitronaphthalene-4:8-disulphonic acid or of 4-chloro-1-nitronaphthalene-8-sulphonic acid (the latter appears to be the sole product of the nitration of 1-chloronaphthalene-5-sulphonic acid; the *sodium* salt is described. It is reduced to 4-chloro- α -naphthylamine-8-sulphonic acid, rhombic crystals, the *sodium* salt of which is sparingly soluble in water). 4:8-Dichloro- α -naphthylamine crystallises in long, slender needles, m. p. 113°, and yields an *acetyl* derivative, m. p. 163°.

5:8-Dichloro-1-nitronaphthalene, m. p. 93° (5:8-dichloro- α -naphthylamine, m. p. 104°, and its *acetyl* derivative, hexagonal prisms, m. p. 202°), is prepared by the chlorination of the product of the nitration of 1-chloronaphthalene-4-sulphonic acid. The production of two isomeric nitro-acids during the latter process is most conclusively demonstrated by their reduction to the

readily soluble 8-chloro-1-aminonaphthalene-5-sulphonic acid (the constitution of which follows from its conversion by sodium amalgam into 8-chloro- α -naphthylamine) and the sparingly soluble 5-chloro-1-aminonaphthalene-8-sulphonic acid, which is converted by boiling its diazotised solution into the *sulphone* (annexed formula), colourless needles, m. p. 184°.



4-Chloro-1:8-dinitronaphthalene, m. p. 180°, is prepared from 1:8-dinitronaphthalene-4-sulphonic acid (the *sodium* salt and the corresponding *sulphonyl chloride*, pale yellow needles, m. p. 152·5°, of the latter are described).

When similarly chlorinated, 1:8-dinitronaphthalene-3:6-disulphonic acid and 1:5-dinitronaphthalene-3:7-disulphonic acid do not yield precipitates.

H. W.

Vapour Pressure Determinations on Naphthalene, Anthracene, Phenanthrene, and Anthraquinone between their Melting and Boiling Points. O. A. NELSON and C. E. SENSEMAN (*J. Ind. Eng. Chem.*, 1922, **14**, 58—62).—Few determinations of vapour pressure have been carried out with most of the solid hydrocarbons between the temperatures of their melting and boiling points, or above. Vapour-pressure determinations over a range of temperatures have now been carried out on naphthalene, anthracene, phenanthrene, and anthraquinone, using Smith and Menzies's dynamic isotenoscope (*A.*, 1910, ii, 1037), and tables and curves of observed vapour pressures of these compounds are recorded. Boiling-point determinations on anthracene, phenanthrene, and anthraquinone gave anthracene, b. p. 342°; phenanthrene, b. p. 340·2°; anthraquinone, b. p. 379·8°.

F. M. R.

Perylene. F. HANSGIRG (U.S. Pat. 1384615; cf. *A.*, 1920, i, 541).—A high yield of perylene is obtained by treating 2-derivatives of naphthalene or of 1:1'-dinaphthyl with halogenating agents such as the halogen compounds of phosphorus, antimony, arsenic, or aluminium to obtain 2-substituted halogen derivatives, and then transforming the latter into perylene by the action of ring-closing reagents such as aluminium chloride or by the "pyrolytic synthesis." A reducing flux such as phosphorous acid is preferably used in the process and it may be carried out as a single operation with isolation of the intermediate halogen derivatives, or, if desired, the latter may be separately obtained and used as starting materials for the last stage of the process. Among the starting materials which may be used are 2:2'-hydroxy-1:1'-dinaphthyl and 2:2'-dichloro-1:1'-dinaphthyl.

CHEMICAL ABSTRACTS.

Condensations of Acetylene. I. Elucidation of the Constitution of Cuprene. H. P. KAUFMANN and M. SCHNEIDER (*Ber.*, 1922, **55**, [B], 267—282).—Cuprene has been obtained previously by several observers by the decomposition of acetylene in the presence of reduced copper or oxides of copper, but the elucidation of its constitution has been rendered difficult by the poverty of the yield, the insolubility of the product, and the

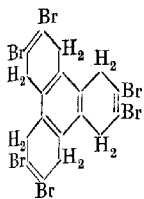
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difficulty with which it is attacked by reagents. A more potent catalyst has now been found in the residue obtained by heating anhydrous copper ferrocyanide in a current of air at 250° during fifteen minutes, which is approximately three times as active as reduced copper. The optimal temperatures for reduced copper, cupric oxide, cuprous oxide, and copper ferrocyanide residue are $240-250^{\circ}$, $230-240^{\circ}$, $230-240^{\circ}$, and $240-250^{\circ}$, respectively. The product of the reaction has a differing colour, dependent on the duration of heating and the particular contact agent. The residue obtained with decomposed copper ferrocyanide is yellow to pale brown, whereas that prepared with other catalysts is darker in shade, the portions richer in copper being dark brown to black. The latter are converted into paler products poorer in copper by further treatment with acetylene. With a short period of heating the product is loose and voluminous, but becomes more compact when the heating is protracted. It is frequently spontaneously inflammable at $100-150^{\circ}$, but this property is not due to cuprene itself, but to finely-divided pyrophoric metal. A liquid condensation product is deposited in green, oily drops on the cooler portions of the tube; the further investigation has been prevented by the small quantity available. Copper can only be removed from the solid product with great difficulty by treatment with hydrochloric acid (20%), and it is necessary to use aqua regia to obtain specimens the copper content of which is so small that it can be neglected in the analysis. The composition of cuprene is not uniform, varying between $(C_{11}H_{10})_x$ and $(C_{15}H_{10})_x$. The main factor in the formation of the different types of cuprene is the uncontrollable oxidative action of the oxygen. The formation of cuprene cannot at present be completely explained, but it appears most probable that a copper acetylide is formed intermediately which decomposes into cuprene without explosion; the uniform distribution of the metal throughout the product is otherwise difficult to account for.

Cuprene is attacked violently by very concentrated nitric acid. It dissolves very slowly in boiling 50% nitric acid, and the clear yellow solution, when neutralised with ammonia and concentrated, yields ammonium mellitate. If the acid solution is diluted largely with water, a brown, mellogen-like precipitate is obtained which is transformed into mellitic acid by nitric acid (80%) and into benzoic acid by dry distillation. The filtrate from the brown precipitate is neutralised by barium hydroxide, whereby an inseparable mixture of barium salts is obtained from which naphthalene is produced by dry distillation. Cuprene is not attacked by dilute solutions of bromine in water or organic media, whereas the action of elementary bromine causes carbonisation with elimination of hydrogen bromide. It may, however, be brominated by heating a paste of it with water and bromine at $100-130^{\circ}$ in the presence of iron bromide. Since cuprene itself is not homogeneous, it is not surprising that the composition of the brominated product depends on the experimental conditions adopted. One such substance, prepared by extracting the crude product with

alcohol and subsequent treatment of the residue from the alcoholic solution with ether, forms a pale yellow, amorphous powder, analyses and determinations of the molecular weight of which agree with the formula $C_{18}H_{12}Br_6$. It is converted by nitric acid into mellitic acid. It appears, therefore, to be a hexabromohexahydrotriphenylene (annexed formula), in which the position of the bromine atoms is not established. All attempts to isolate the parent hydrocarbon by removal of the bromine atoms were unsuccessful, since the residue (immediately after loss of bromine) became polymerised to a hydrocarbon resembling cuprene.



H. W.

The System : Acetanilide-Water. N. SCHOORL and F. N. B. DE WEERD (*Rec. trav. chim.*, 1922, **41**, 15—20).—The acetanilide-water system exhibits a region of heterogeneous equilibrium which is situated above the ordinary temperature and connects the solubility and depression of freezing-point curves. The temperature limits of this region are 83.2° and 144° , and the composition limits from 5.2% to 87% of acetanilide. At 144° , the highest temperature at which the system is heterogeneous, the composition is 40% acetanilide, 60% water.

H. J. E.

Aniline Glucoside (Glucose Anilide). TH. SABALITSCHKA (*Ber. deut. Pharm. Ges.*, 1921, **31**, 439—445).—Acetobromoglucose reacts with aniline at ordinary temperatures, and after twenty-four hours the initially clear solution sets to a solid mass from which *aniline tetractyl-d-glucoside* was isolated in long needles, m. p. $95-96^\circ$, $[\alpha]_D^{25} -59.5$ (after twenty-four hours). On hydrolysis in methyl alcoholic solution with barium hydroxide, it was converted into *aniline-d-glucoside*, which accordingly has the γ -oxidic structure $OH \cdot CH_2 \cdot CH(OH) \cdot CH \cdot CH(OH) \cdot CH(OH) \cdot CH \cdot NHPh$. The

substance was deposited from organic solvents as a gelatinous mass which dried to a white, amorphous powder, m. p. 147° , $[\alpha]_D^{25} -52.4^\circ$ (in methyl alcohol) constant after four days. *Aniline-d-glucoside* thus prepared was identical with glucose anilide, obtained by the direct action of aniline on dextrose, to which the structure of a Schiff's base had originally been ascribed, and the correctness of Sorokin's (A., 1888, 807) and, later, of Irvine's views (T., 1908, 93, 95, 1429) of the constitution of this substance as a glucoside is thus confirmed.

G. F. M.

6-Amino- α -naphthol-5-sulphonic Acid (A-acid) and its Derivatives. HANS TH. BUCHERER and RUDOLF WAHL (*J. pr. Chem.*, 1921, [ii], **103**, 129—162).—2-Naphthylamine-1 : 5-disulphonic acid, which may be obtained by treating 2-naphthylamine-1-sulphonic acid with fuming sulphuric acid at $30-40^\circ$, is converted into its potassium salt and fused with potassium hydroxide to give 6-amino- α -naphthol-5-sulphonic acid (A-acid). The yield

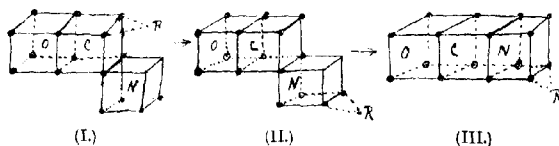
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and nature of the by-products (6-amino- α -naphthol, 1:6-dihydroxy-naphthalene, and 1:6-dihydroxynaphthalene-5-sulphonic acid) vary with the exact conditions employed. 4-acid forms a characteristic orange diazonium salt. 2-Naphthylamine-1:5-disulphonic acid, on heating with 75% sulphuric acid, gives β -naphthylamine and 2-naphthylamine-5-sulphonic acid and with sulphuric acid monohydrate, 2-naphthylamine-5-, -6-, and -7-sulphonic acids. 4-acid with mineral acids gives 6-amino- α -naphthol. On sulphonation with concentrated sulphuric acid a mixture of 6-amino- α -naphthol-2:5-disulphonic acid and 6-amino- α -naphthol-4:5-disulphonic acid are obtained. With acetic anhydride, 6-acetyl-amino- α -naphthol-5-sulphonic acid is formed, with benzoyl chloride 6-dibenzoylamino- α -naphthol-5-sulphonic acid, with toluenesulphonyl chloride it forms the expected product, $C_{17}H_{15}O_6NS_2$, and with carbonyl chloride the carbamide.

W. O. K.

Rearrangements of some New Hydroxamic Acids Related to Heterocyclic Acids and to Diphenyl- and Triphenyl-acetic Acids.

LAUDER W. JONES and CHARLES D. HURD (*J. Amer. Chem. Soc.*, 1921, **43**, 2422-2448).—An interpretation of the mechanism of the Beckmann rearrangement is proposed, based on Langmuir's theory of the atom. The stages in the rearrangement are pictured as follows, in which Fig. 1 represents the intermediate




univalent nitrogen derivative and Fig. III the carbimide stage in the rearrangement. As a further hypothesis to explain why one radicle, R, will migrate more readily than another radicle, R', the authors suggest that the relative ease of arrangements of the Beckmann type is dependent on the tendency for the radicle R, in the univalent nitrogen derivative, such as $[R\cdot CO\cdot N]$, to exist as a free radicle. This hypothesis finds support in the results obtained for the relative ease with which the sodium and potassium salts of the acyl esters of diphenylacethydroxamic acid and triphenylacethydroxamic acid undergo rearrangement. The salts of the triphenyl derivative undergo rearrangement the more readily.

Two new methods of preparing hydroxamic acids are described. In the first, by the action of free hydroxylamine on a keten such as diphenylketen, the corresponding hydroxamic acid is obtained, $CPh_2\cdot CO + NH_2\cdot OH = CHPh_2\cdot CO\cdot NH\cdot OH$.


The second method is a modification of the one usually employed, namely, the action of acid chlorides on hydroxylamine in aqueous solution. If a neutral solvent, such as benzene, is used in place of water, a quantitative yield of the monohydroxamic acid is obtained.

Diphenylacetylhydroxamic acid, $\text{CHPh}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$, m. p. 172° , is prepared by the action of hydroxylamine on ethyl diphenylacetate in the presence of sodium methoxide or by either of the above methods. It gives a *benzoyl* ester, m. p. 140 — 140.5° , the *sodium* and *potassium* salts of which could not be obtained in the pure state. The *silver* salt showed chromoisomerism. The alcohol-ether solution of the sodium salt, on evaporation, leaves a mixture of the salt with its products of decomposition and rearrangement, namely, *diphenylmethylcarbimide*, *diphenylmethylurethane*, m. p. 122 — 123° , and sodium benzoate. When this residue is extracted with cold water and the solution filtered and boiled, *s-bisdiphenylmethylcarbamide*, $\text{CO}(\text{NH}\cdot\text{CHPh}_2)_2$, m. p. 269.5 — 270° , is obtained. Diphenylacetylhydroxamic acid yields a *monoacetyl* derivative, m. p. 113 — 113.5° ; giving *potassium*, *sodium*, and *silver* salts, and a *diacetyl* derivative, m. p. 95.5 — 97.5° . Diphenylmethyl urethane reacts with phosphorus pentachloride, yielding *diphenylmethylcarbonyl chloride*, $\text{CHPh}_2\cdot\text{NH}\cdot\text{COCl}$, which when left in contact with calcium oxide gives diphenylmethylcarbimide and this when treated with benzoyl-hydroxylamine yields *s-bisdiphenylmethylcarbamide*. *

Triphenylacetyl chloride reacts with hydroxylamine to give *triphenylacetylhydroxamic acid*, m. p. 175 — 176° , which yields a *benzoyl* ester giving *sodium*, *potassium*, and *silver* salts. The *silver* salt showed chromoisomerism, but the *sodium* and *potassium* salts could not be obtained pure owing to the readiness with which they decomposed, giving *triphenylmethylcarbimide*, m. p. 85 — 87° . The *acetyl* ester, m. p. 133.5 — 134° , gives *potassium*, *sodium*, and *silver* salts, the two former of which are somewhat more stable than the corresponding salts of the *benzoyl* ester. In these rearrangements, none of the *s-bistriphenylmethylcarbamide* was formed.

Pyromueylhydroxamic acid,  $\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$ (cf. Pickard and

Neville, T., 1901, 79, 847), its *ammonium* salt, m. p. 130 — 131° , its *benzoyl* ester, m. p. 140° , and the *potassium*, *sodium*, and *silver* salts of the ester were prepared. When the *potassium* salt was warmed in aqueous solution, some of the ester was first precipitated, and when this was filtered off and the filtrate boiled, a red, resinous mass, presumably of difurylcarbamide, was obtained. The *acetyl* ester, m. p. 95 — 96° , of the hydroxamic acid gave *potassium*, *sodium*, and *silver* salts, the rearrangement and hydrolysis of these salts being similar to those of the corresponding salts of the *benzoyl* ester.

Thienoylhydroxamic acid,  $\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$, m. p. 123 — 124.5° , was

obtained either by the action of hydroxylamine on ethyl thiophenecarboxylate, $\text{C}_6\text{H}_4\text{S}\cdot\text{CO}_2\text{Et}$, or by the action of hydroxylamine on thienoyl chloride. It gave an *ammonium* salt, m. p. 142 — 143° (decomp.); a *benzoyl* ester, m. p. 143 — 144° , giving *potassium*, *sodium*, and *silver* salts; an *acetyl* ester, m. p. 96.5 — 97° , giving *potassium*, *sodium*, and *silver* salts; and a *thienoyl* ester [*dithienoyl*-

hydroxamic acid, $C_6H_5S\cdot CO\cdot NH\cdot O\cdot CO\cdot C_6H_5$], which occurred in two forms, and gave *potassium*, *sodium*, and *silver* salts.

The salts of the esters of thienoylhydroxamic acid underwent slight hydrolysis in aqueous solution, but the main change was one of rearrangement to *sym*-dithienylcarbamide.

The *thienoyl* ester, m. p. 133—133.5°, of benzhydroxamic acid, which was isomeric with the benzoyl ester of thenhydroxamic acid, was prepared and its *potassium* and *silver* salts were investigated. The melting points of the esters and the decomposition temperatures of their salts, and the ease of rearrangement of the latter, were almost identical in the two cases.

W. G.

Metallic Derivatives of Nitrophenolic Compounds. IV. Some Complex Nitrophenoxides of Magnesium, Silver, and Lead. ARCHIBALD EDWIN GODDARD and JAMES BERTRAM WARD (T., 1922, 121, 262—266).

Auto-oxidation : the Anti-oxygens. CHARLES MOUREU and CHARLES DUFRASSE (*Compt. rend.*, 1922, 174, 258—264).—The auto-oxidation of a large number of substances may be checked by the presence of traces of certain compounds to which the authors give the name "anti-oxygens." Most of the substances which have been found to show this inhibiting action belong to the phenol group, and of these quinol, catechol, and pyrogallol are particularly active. This protecting action may be prolonged for two years at least, providing the substance capable of auto-oxidation does not sublime from the anti-oxygen. The secondary reactions which often accompany auto-oxidation are also inhibited by the presence of the anti-oxygens. The action of the anti-oxygens is apparently catalytic, and it is of interest to note that traces of pyrogallol, a substance commonly used as an absorbent of oxygen, oppose the action of this gas.

The bearing of these observations on the phenomena of life in the animal and the vegetable kingdom is discussed. It is suggested that the toxic properties of phenols are connected with their activities as anti-oxygens.

W. G.

The Quadrivalence of Tin in its Mercaptides. H. WUYTS and A. VANGINDERTAELEN (*Bull. Soc. chim. Belg.*, 1921, 30, 323—328).—Stannic mercaptides can be prepared (a) by the action of tin and hydrochloric acid on organic disulphides with subsequent neutralisation, (b) from a thioalcohol and stannous chloride in presence of air, or (c) from a thioalcohol and stannic chloride. Attempts to prepare stannous mercaptides did not succeed, and the behaviour of tin in this respect is compared with that of its sulphides towards alkali sulphide solutions.

The *mercaptide*, $Sn(S\cdot C_6H_4\cdot NMe_2)_4$, prepared from dimethylaniline-disulphide, is a red, crystalline substance, m. p. 159°; with benzoyl chloride in benzene solution, it forms the benzoate of the corresponding thioalcohol, m. p. about 136°; with methyl iodide, two reactions take place, one with the rupture of the sulphur-tin linking

and the combination of methyl and iodine with the elements respectively, the other with formation of the iodide of the quaternary ammonium base, $\text{NMe}_3\text{I}\cdot\text{C}_6\text{H}_4\cdot\text{SMe}$. Similarly, from di-*p*-aminophenyl disulphide, the *mercaptide*, $\text{Sn}(\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_4$, red, leafy crystals, m. p. about 166° , was obtained. H. J. E.

Sulphobenzide [Diphenylsulphone]. EUG. GRANDMOUGIN (*Compt. rend.*, 1922, 174, 168—170).—3 : 3'-Diaminodiphenylsulphone gives a bis-diazo-derivative which couples normally with the naphthols and their sulphonic derivatives. The dyes obtained have almost the same shades as the corresponding dyes from aniline itself, the chromophoric influence of the sulphone group in the meta-position to the two amino-groups being thus practically negligible. The dyes obtained dye only wool and not cotton.

New compounds mentioned are 3 : 3'-*dichlorodiphenylsulphone*, m. p. 108° ; 3 : 3'-*ditromodiphenylsulphone*, m. p. 119° ; and 3 : 3'-*diiododiphenylsulphone*, m. p. 158° .

In view of the erroneous statements occurring in the literature, the correct melting points of certain of the 3 : 3'- and 4 : 4'-derivatives of diphenylsulphone are tabulated as follows.

	(NO ₂) ₂	(NH ₂) ₂	(NHAc) ₂	(OH) ₂	Cl ₂	Br ₂	I ₂
3 : 3'	201°	168°	211°	186—187°	108°	119°	158°
4 : 4'	282	174	280	230	147	172	197

W. G.

Cholesterol Dibromide. I. LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1921, 114, 286—289).—Cholesterol dibromide prepared by the ether method has m. p. $93—94^\circ$, whilst when the glacial acetic acid method is used it has m. p. $110—111^\circ$. The author brings forward evidence which suggests that a compound of the dibromide and acetic acid has been formed in the second case.

The author considers that the cholesterol dibromide, m. p. 122° , obtained by Windaus and Lüders is possibly an isomeride of the dibromide obtained by himself. S. S. Z.

The Replacement of Halogen in 4-Chloro-3-nitrobenzonitrile and in 4-Bromo-3-nitrobenzonitrile. TH. J. F. MATTAAR (*Rec. trav. chim.*, 1922, 41, 24—37).—The reactions between 4-chloro-3-nitrobenzonitrile and/or 4-bromo-3-nitrobenzonitrile and sodium methoxide, sodium ethoxide, sodium phenoxide, methylamine, ethylamine, dimethylamine, aniline, *o*-toluidine, *m*-toluidine, *p*-toluidine, methylaniline, *p*-phenylenediamine, hydrazine, phenylhydrazine, and phenylmethylhydrazine have been investigated. The following new substances have been prepared : 3-Nitro-4-methoxybenzonitrile, pale brown needles, m. p. 151° ; 3-nitro-4-ethoxybenzonitrile, white needles, m. p. 121° ; 3-nitro-4-phenoxybenzonitrile, colourless prisms, m. p. 138° ; 3-nitro-4-methylaminobenzonitrile, yellow needles, m. p. 169° ; 3-nitro-4-ethylaminobenzonitrile, yellow needles, m. p. 132° ; 3 : 5-dinitro-4-ethylnitroaminobenzonitrile, lustrous plates, m. p. 142.5° ; 3-nitro-4-dimethylaminobenzonitrile, yellow plates, m. p. 114° ; 3-nitro-4-*o*-toluidinobenzonitrile, brownish-yellow plates, m. p. 116° ; 3-nitro-4-*m*-toluidino-

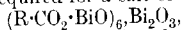
benzonitrile, orange needles, m. p. 149°; *3-nitro-4-p-toluidinobenzonitrile*, orange needles, m. p. 128°; *3-nitro-4-methylanilinobenzonitrile*, yellow, irregular plates, m. p. 144°; *3-nitro-4-p-aminobenzonitrile*, deep violet crystals, m. p. 158°; *benzaldehyde-2-nitro-4-cyanophenylhydrazone*, red plates which turn colourless on drying, m. p. 225°; *acetophenone-2-nitro-4-cyanophenylhydrazone*, lustrous, red needles, m. p. 232°; *3-nitro-4-phenylmethylhydrazinobenzonitrile*, red crystals, m. p. 132°. The reaction between phenylhydrazine and 4-chloro-3-nitrobenzonitrile (cf. Borsche, Stackmann, and Makaroff-Semljansky, A., 1917, i, 15) yields a substance which is considered to be converted on oxidation into 3-nitro-4-phenylhydrazinobenzonitrile, colourless needles, m. p. 181°.

H. J. E.

Preparation of Phenylglycine Compounds. BRITISH DYE STUFFS CORPORATION, LTD., HERBERT LEVINSTEIN, and GEORGES IMBERT (Brit. Pat. 173540).—Phenylglycine compounds are obtained in one operation from trichloroethylene by heating it in aqueous suspension with aniline, and an alkali, preferably calcium hydroxide, in an autoclave at 140–190°, the treatment being continued until the intermediate products, for example, ethylenetriphenyltriamine, are completely transformed into phenylglycine compounds. For example, 132 parts of trichloroethylene, 100 parts of lime, 800 parts of water, and 280 parts of aniline, are heated in an autoclave with constant agitation for twenty-four hours at 180°. The excess of aniline is distilled off the calcium phenylglycine and excess of lime separated from the mother liquors, and converted into sodium phenylglycine by boiling with the requisite quantity of sodium carbonate.

G. F. M.

The Hydrolytic Decomposition of the Bismuth Salts of Phenolcarboxylic Acids. A. PERLING (*Ber. Deut. Pharm. Ges.*, 1921, **31**, 433–438).—The hydrolysis by water of the neutral and basic bismuth salts of benzoic, salicylic, protocatechuic, gallic, and cinnamic acids proceeds to a definite limit which is attained when they are heated at 100° with four consecutive quantities of water for a total of ten hours. Both the neutral and basic salts of the various acids eventually attain the same composition, the only salt remaining unchanged being the basic benzoate, having the composition $(\text{PhCO}_2\cdot\text{BiO})_6\cdot\text{Bi}_2\text{O}_3$. The experimentally-determined composition of the final hydrolytic product of all the other bismuth salts above mentioned was found to be in close agreement with the theoretical figure required for a salt of the composition



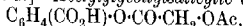
analogous to the basic benzoate (R=phenol residue), and it is therefore evident that hydrolysis proceeds to precisely the same point with all the salts. When shaken at 37° with 0.25% hydrochloric acid, conditions resembling those existing in the stomach, a slightly greater degree of hydrolysis was observed.

G. F. M.

Substituted Salicylic Acids. I. H. P. KAUFMANN and W. KAUFMANN (*Ber.*, 1922, **55**, [B], 282–288).—A number of

substances are described which were obtained during an investigation of the influence of different substituents on the physiological action of salicylic acid.

[With H. Görring].—*Acetylglucosylsalicylic acid*,

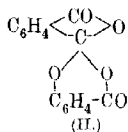


small, colourless needles, m. p. 103–104°, is prepared by the action of acetylglucosyl chloride on sodium salicylate in the presence of benzene at the atmospheric temperature. It is readily hydrolysed by warm water to acetylglucolic and salicylic acids.

The action of *s-o*-phthalyl chloride on sodium salicylate in the presence of boiling dry benzene leads to the formation of a substance (annexed formulæ I or II), colourless needles, m. p. 158.5°. It is slowly hydrolysed by alcoholic sodium hydroxide solution to phthalic and salicylic acids. It is



(I.)



(II.)

reduced by zinc dust and glacial acetic acid to phthalide and salicylic acid; the latter reaction appears to indicate the unsymmetrical constitution of the parent substance, but this point cannot yet be regarded as established with certainty. H. W.

Glucosides. X. The Action of *dl*-Acetobromoglucose on the Silver Salt of *dl*-Mandelic Acid.

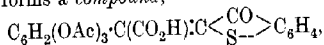
P. KARRER, C. NÄGELI, and ALEX. P. SMIRNOV (*Helv. Chim. Acta*, 1922, 5, 141–146).—It has been shown previously (Karrer and Nägeli, A., 1919, i, 594) that acetobromoglucose reacts with silver *dl*-mandelate in the presence of toluene to form *d*-tetra-acetylglucosido-*dl*-mandelic acid, $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}_2\text{Ac}_2$, *d*-tetra-acetylglucose *dl*-mandelate, and *d*-tetra-acetylglucose *d*-tetra-acetylglucosido-*l*-mandelate from which *l*-mandelic acid was isolated by hydrolysis. The similar action between *dl*-acetobromoglucose and silver *dl*-mandelate has been found to give products of the same three types, all of which are optically inactive. Since *d*-acetobromoglucose only combines with *l*-mandelic acid to form a corresponding compound (*loc. cit.*), it follows that the inactive tetra-acetylglucose tetra-acetylglucosidomandelate must be a racemate combined from *d*-tetra-acetylglucose *d*-tetra-acetylglucosido-*l*-mandelate and *l*-tetra-acetylglucose *l*-tetra-acetylglucosido-*d*-mandelate. Reaction thus appears to be unusually selective, the *d*-glucose derivative combining only with the *l*-acid in this manner, whereas the *l*-glucose compound unites with the *d*-acid. A satisfactory explanation of the unusually marked effect of configuration on the reaction cannot at present be given.

l-Acetobromoglucose, colourless needles, m. p. 88°, $[\alpha]_D^{25} -192.7^\circ$, in ethereal solution, is prepared by the action of acetyl bromide and glacial acetic acid on *l*-glucose. When mixed in ethereal solution with an equal quantity of *d*-acetobromoglucose, it gives *dl*-acetobromoglucose, colourless needles, m. p. 85°. *dl*-Tetra-acetylglucose *dl*-mandelate and *dl*-tetra-acetylglucose *dl*-tetra-acetylglucosido-*dl*-mandelate have m. p. 146° and 227°, respectively. H. W.

k*

New Synthesis of Hydroxylated Benzoylformic [Phenylglyoxylic] Acids. H. FINGER and LINA EIRICH (*J. pr. Chem.*, 1921, [ii], **103**, 249—252).—Ethyl cyanofornate can be used instead of hydrocyanic acid in the Gattermann aldehyde synthesis, and hydroxylated phenylglyoxylic acids are produced. Pyrogallol and methyl cyanofornate, dissolved in ether, give with zinc chloride and gaseous hydrogen chloride 2:3:4-trihydroxyphenylglyoxylic acid, $C_6H_2(OH)_3 \cdot CO \cdot CO_2H$, m. p. 171° , which dyes chrome-mordanted wool. It gives a sodium salt, $C_6H_2O_6Na$; a normal aniline salt, m. p. 138° ; whilst on heating with aniline at 135° , 2:3:4-trihydroxybenzylideneaniline, $C_6H_2(OH)_3CH:NPh$, is formed, thus proving the constitution of the acid.

The following derivatives of 2:3:4-trihydroxyphenylglyoxylic acid are also described: *nitrophenylhydrazone*, yellowish-red needles, m. p. 230 — 240° (decomp.); *semicarbazone*, decomp. 230° . With oxythionaphthen dissolved in acetic anhydride, trihydroxyphenylglyoxylic acid forms a compound,



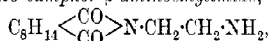
and it couples with benzenediazonium chloride to give an azo-dye.
W. O. K.

The Preparation of Chloro- and Bromo-tyrosine and the Analogous Tyramines. R. ZEYNEK (*Z. physiol. Chem.*, 1921, **114**, 275—285).—3:5-Dibromotyrosine and 3:5-dichlorotyrosine are best prepared by the action of the respective halogens on *l*-tyrosine suspended in glacial acetic acid.

3:5-Dichlorotyrosine has m. p. 256 — 260° (decomp.), crystallises in rhombic platelets, and the anhydrous hydrochloride gives in 5% aqueous solution $[z]_D^{20} -7.8^\circ$; in 4% hydrochloric acid, $[z]_D^{20} -2.9^\circ$. A 5% solution of dichlorotyrosine containing $2H_2O$ dissolved in 4% hydrochloric acid gave $[z]_D^{20} -2.8^\circ$. *p*-Hydroxyphenylethylamine, when suspended in glacial acetic acid and brominated, yields dibromotyramine hydrobromide, crystallising in monoclinic platelets, m. p. 270° . The free base crystallises in white, flat, rhombic rods, m. p. 210° . Dichlorotyramine hydrochloride, prepared similarly, crystallises in monoclinic plates, m. p. 284 — 286° ; the base has m. p. 219 — 222° .
S. S. Z.

Preparation of Soluble Derivatives of Camphoric Acid. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 173063).—Soluble derivatives of camphor which retain the therapeutic properties of that substance but give stable solutions in water sterilisable by heat and therefore suitable for subcutaneous injection, are exemplified by certain *N*-substituted derivatives of camphorimide of the type $C_8H_{14} < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > N \cdot R \cdot N < \begin{smallmatrix} R' \\ R'' \end{smallmatrix}$, where R is an alkyl or alkylene group, and R' and R'' are hydrogen, alkyl, or alkylene groups. These compounds are obtainable from camphorimide by the usual methods, as, for example, by causing its isolated dry salt or a solution* to react with polyhalogenised saturated or unsaturated aliphatic hydrocarbons or with halogen hydrins, and

the *N*-halogen alkyl or *N*-halogen alkylene camphorimide thus obtained (after substituting halogen for hydroxyl if a halogen-hydrin has been used) is treated with ammonia or an alkylamine. Or, alternatively, camphoric acid or its anhydride may be caused to react with a diamine of the type $\text{NH}_2\cdot\text{R}\cdot\text{NR}'\text{R}''$. The following substances are described: *Camphor-β-hydroxyethylimide*, a thick, colourless oil, b. p. $190^\circ/15$ mm., is prepared by the action of ethylene iodohydrin on sodiocamphorimide in absolute alcoholic solution. *Camphor-β-chloroethylimide*, prepared by the action of phosphorus pentachloride on the above, is a pale yellow oil, b. p. $168^\circ/10.5$ mm. By heating with ammonia at 100° under pressure, it is converted into *camphor-β-aminoethylimide*,



which can be isolated as its *hydrobromide* as an incompletely solidifying syrup which decomposes at $135\text{--}140^\circ$. The chloroethylimide, when similarly heated with 33% dimethylamine solution at $120\text{--}125^\circ$, gives *camphor-β-dimethylaminoethylimide*, b. p. $163^\circ/14$ mm. It forms a crystalline *hydrobromide*, m. p. 207° , soluble in both water and alcohol. *Camphor-β-bromoethylimide* is obtained by heating potassium camphorimide with an excess of ethylene dibromide on an oil-bath. It boils at $186^\circ/12$ mm. When heated at 100° with diethylamine, it is converted into *camphor-β-diethyl-aminoethylimide*, a viscid oil, b. p. $183\text{--}185^\circ/12$ mm., which gives a crystalline *hydrobromide*, m. p. 157° . *Camphor-β-allyl-aminoethylimide* is similarly prepared from allylamine and the halogenethylimide. It boils at $187^\circ/12$ mm., and gives a *hydrobromide* crystallising in fine leaflets, m. p. 144° . Illustrative of the second general method of preparation, the above-mentioned β-diethylaminoethylimide may also be obtained by heating at $180\text{--}200^\circ$ camphoric acid and *as-diethylethylenediamine*. The latter substance, obtained by the reduction of diethylaminoacetonitrile with sodium and alcohol, forms an oil, b. p. $140\text{--}145^\circ$, with strongly basic properties. In a similar way, from the reduction product of piperidine acetonitrile, by heating with camphoric acid, the corresponding imide *camphor-β-piperidylethylimide* is obtained. Its *hydrobromide* crystallises in fine, felted needles, m. p. 193.5° . G. F. M.

The Bile Acids. III. Biloidanic Acid [Letsche's Acid].

W. BORSCHKE, O. WEICKERT, and ROBERT MEYER (*Ber.*, 1921, 54, [B], 3177—3182).—Biloidanic acid has been prepared by Letsche (*A.*, 1909, i, 697) by the action of a mixture of nitric and sulphuric acids on cholic acid, and examined subsequently by Schenk (*A.*, 1920, i, 847; 1921, i, 179), who concurs in ascribing to it the formula $\text{C}_{16}\text{H}_{28}\text{O}_{10}$. Specimens of the purified acid examined by the authors did not give analytical results in agreement with this formula. The acid was therefore esterified with methyl alcohol and hydrogen chloride, but the product, mainly a dimethyl trihydrogen ester, was not quite uniform. It was therefore converted by diazomethane into the pentamethyl ester (which

has also been prepared by Schenck from the silver salt and methyl iodide). The latter cannot be satisfactorily purified by crystallisation, but, after being distilled under diminished pressure gives analytical results in agreement with the formula $C_{23}H_{36}O_{10}$, thus indicating the formula $C_{15}H_{26}O_{10}$ for the parent acid. The pentamethyl ester has m. p. $91-92^\circ$ after softening at 87° , b. p. $321-322^\circ/18$ mm., $[\alpha]_D$ about $+20^\circ$ in absolute alcoholic solution. Direct analysis of the acid regenerated from the hydrogen ester leads to the same result. The pentamethyl ester has not yet been smoothly re-converted into the acid.

A modification of Letsche's method of preparing the acid is described which permits the isolation of biloidanic acid in the pure condition after a single crystallisation. H. W.

A Critical Examination of the Aromatic Aldehydes occurring in certain Eucalyptus Oils. ARTHUR RAMON PENFOLD (T., 1922, 121, 266-269).

The Reduction of Naphtholcarboxylic Acids to Aldehydes. HUGO WEIL and WALTER HEERDT (*Ber.*, 1922, 55, [B], 224-230).—A continuation of previous work (Weil and Ostermaier, this vol., i, 139).

Tetrahydronaphthaldehyde has been obtained previously (*loc. cit.*) by the reduction of β -naphthol-3-carboxylic acid by sodium amalgam in boric acid solution with the addition of a neutral mixture of sodium sulphite and sodium hydrogen sulphite. The same result is obtained when the action is effected at a temperature not exceeding -5° . The aldehyde is also obtained by the reduction of 2-acetoxynaphthalene-3-carboxylic acid, 1-amino- β -naphthol-3-carboxylic acid, and 1-bromo- β -naphthol-3-carboxylic acid, ammonia or hydrogen bromide respectively being eliminated from the compounds last named. Tetrahydronaphthaldehyde hydrazone, after being crystallised from alcohol containing a little glacial acetic acid, has m. p. 106.5° instead of 96.5° as previously recorded (*loc. cit.*). 1-Amino- β -naphthol-3-carboxylic acid is prepared conveniently by coupling β -naphthol-3-carboxylic acid with diazotised sulphanilic acid and reduction of the dye so formed with zinc dust and glacial acetic acid.

α -Naphthol-2-carboxylic acid does not appear to be reduced beyond the 1-hydroxynaphthal-2-aldehyde stage even by energetic treatment at 25° , 40° , or 55° .

4-Amino-1-hydroxynaphthalene-2-carboxylic acid is so feebly acidic that it is precipitated from solutions of its salts by boric acid and thus escapes reduction.

4-Sulpho-1-hydroxynaphthalene-2-carboxylic acid is reduced to α -naphthol-2-aldehyde, the sulphonic group being eliminated. On the other hand, the cautious reduction of 4-bromo-1-hydroxynaphthalene-2-carboxylic acid leads to the formation of 4-bromo-1-hydroxynaphthalene-2-aldehyde, which, however, could not be obtained in the homogeneous state. It gives the normal compounds with phenylhydrazine (yellow leaflets, m. p. 159°), aniline (orange-yellow needles, m. p. 161°), o-toluidine (yellowish-red

needles, m. p. 188°), *p*-toluidine (yellowish-red needles, m. p. 171°), benzidine ($C_{23}H_{17}ON_2Br$, red leaflets, m. p. 218°), α -naphthylamine (red needles, m. p. 196°), *o*-phenylenediamine ($C_{12}H_{10}ON_2Br$, m. p. 225°), *m*-phenylenediamine (m. p. 201°), *p*-phenylenediamine (m. p. 198°); with ammonia, it gives the compound, $C_{22}H_{18}O_3N_2Br_2$, yellow crystals, m. p. 126°.

4-Chloro-1-hydroxynaphthalene-2-carboxylic acid, m. p. 228°, prepared by the passage of chlorine into a solution of α -naphthol-2-carboxylic acid in glacial acetic acid, is reduced similarly to 4-chloro-1-hydroxynaphthalene-2-aldehyde. The latter gives the usual derivatives with hydroxylamine (colourless needles, m. p. 184°), hydrazine (yellow needles, m. p. 179°), phenylhydrazine (yellow leaflets, m. p. 153°), aniline (yellow needles, m. p. 157°), *o*-toluidine (orange-yellow crystals, m. p. 183°), *p*-toluidine (orange-yellow crystals, m. p. 164°), α -naphthylamine (reddish-yellow leaflets, m. p. 188°), benzidine ($C_{23}H_{17}ON_2Cl$, red crystals, m. p. 214°), *o*-phenylenediamine ($C_{12}H_{10}ON_2Cl$, leaflets, m. p. 221°), *m*-phenylenediamine (m. p. 250°), *p*-phenylenediamine (m. p. 244°); with ammonia it gives the compound, $C_{32}H_{18}O_3N_2Cl_2$. The sodium compound of 4-chloro-1-hydroxynaphthalene-2-aldehyde crystallises in yellow leaflets.

H. W.

Preparation of Hydroxyaldehydes and their Derivatives.

SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat. 164715).—In the manufacture of aromatic hydroxyaldehydes by the process described in Brit. Pat. 161679 (A., 1921, i, 420) equally good results are obtained without the use of an organic solvent. Thus vanillin is obtained by adding a concentrated solution of 5.3 kilos. of sodium nitrite and, after some time, 4 kilos. of guaiacol and 8 kilos. of 40% formaldehyde solution to a solution of 8 kilos. of dimethylaniline in 33 kilos. of hydrochloric acid in presence of 33 kilos. of ice. A low temperature is maintained for some hours and the reaction is completed on a water-bath.

G. F. M.

The Melting Points of certain Fatty-aromatic Ketones.

RIKO MAJIMA, KWANTO NAGAOKA, and KEISUKE TAMADA (*Ber.*, 1922, 55, [B], 215—217).—A number of ketones of the types $C_6H_3(OMe)_2CO\cdot R$, $C_6H_4(OMe)CO\cdot R$, and $C_6H_5CO\cdot R$ have been prepared. The melting points of a compound with an even number of carbon atoms in the side-chain is invariably higher than that of either of its immediate neighbours with an odd number of carbon atoms, as shown by the annexed table:

Side-chain.	M. p. of the compounds.		
$CO\cdot R$	$C_6H_3(OMe)_2CO\cdot R$	$C_6H_4(OMe)CO\cdot R$	$C_6H_5CO\cdot R$
$CO\cdot C_{10}H_{21}$		49°	
$CO\cdot C_{11}H_{23}$	68—69°	62.5	45°
$CO\cdot C_{12}H_{25}$	59.5—60	59	41—42
$CO\cdot C_{13}H_{27}$	74—75	67	54—55
$CO\cdot C_{14}H_{29}$	64—65	65—66	50—51
$CO\cdot C_{15}H_{31}$	79—80	72—73	59—60
$CO\cdot C_{16}H_{33}$	67—68	70.5	56—56.5
$CO\cdot C_{17}H_{35}$	82—83	77—77.5	

H. W.

Elimination of Hydrogen from Aromatic Nuclei and Union of the Latter by means of Aluminium Chloride. ROLAND SCHOLL and CHRISTIAN SEER (*Ber.*, 1922, 55, [B], 109—117; cf. A., 1913, i, 56, 734).—Previous attempts to convert *o*-chlorophenyl α -naphthyl ketone into 5-chloro-1:9-benzanthrone were unsuccessful; this does not, however, appear to be a general characteristic of chlorophenyl ketones, since the corresponding meta- and para-compounds give substituted benzanthrones in rather poor yield.

[With JOSEF DALMER.]—*o*-Chlorophenyl- α -naphthyl ketone crystallises in colourless needles, m. p. 82°.

m-Chlorophenyl- α -naphthyl ketone, small, pale yellow prisms, m. p. 77–79°, is obtained by the action of *m*-chlorobenzoyl chloride on naphthalene in the presence of carbon disulphide and aluminium chloride. It is converted by aluminium chloride at 145° into 6-chloro-1:9-benzanthrone, golden-yellow needles, m. p. 186–187°. The constitution of the latter follows from the observation that it is oxidised by chromic acid to 6-chloroanthraquinone-1-carboxylic acid, lustrous, golden needles, m. p. 295°, which loses carbon dioxide at 310–320° and yields 2-chloroanthraquinone, slender, yellow needles, m. p. 203–204°.

p-Chlorophenyl α -naphthyl ketone, colourless rods, m. p. 126–128°, is converted by aluminium chloride into 7-chloro-1:9-benzanthrone, yellow, microscopic crystals, m. p. 187–188°.

Anthraquinone-1-carboxyl chloride, pale yellow needles, m. p. 203–204° (cf. Schaarschmidt, A., 1915, i, 566), is conveniently prepared by boiling a solution of the carboxylic acid in phosphoryl chloride with a slight excess of phosphorus pentachloride. It is converted by naphthalene and aluminium chloride in the presence of nitrobenzene into α -naphthyl 1-anthraquinonyl ketone, m. p. 231–232°. Attempts to prepare a benzanthrone derivative from the latter were unsuccessful.

H. W.

Syntheses by means of Sodamide. IX. The Preparation of $\beta\beta$ -Dialkyl- α -hydrindones or 2:2-Dialkylindan-1-ones. ALBIN HALLER and EDOUARD BAUER (*Ann. Chim.*, 1921, [ix], 16, 340–354).—The chlorides of β -phenyl- $\alpha\alpha$ -dialkylpropionic acids, $\text{CH}_2\text{Ph}\cdot\text{CR}_2\cdot\text{CO}_2\text{H}$, behave like β -phenylpropionyl chloride (cf. Kipping, T., 1894, 65, 480) in the presence of aluminium chloride, giving 2:2-dialkylindan-1-ones, which themselves react with sodamide to give the amide corresponding with the original acid chloride.

β -Phenyl- $\alpha\alpha$ -dimethylpropionic acid reacts with thionyl chloride, giving the acid chloride, m. p. 5°; b. p. 125–126°/15 mm., which when treated in the cold with aluminium chloride gives 2:2-dimethylindan-1-one, $\text{C}_6\text{H}_4\langle\text{CH}_2\text{CO}\rangle\text{CMe}_2$, m. p. 44–45°; b. p. 118–119°/15 mm., giving a semicarbazone, m. p. 209–210°. The indanone is decomposed by sodamide, giving β -phenyl- $\alpha\alpha$ -dimethylpropionamide, and since the alkylated indanone may be prepared from indanone itself by the action of methyl iodide on its sodium

derivative, this furnishes a new method for preparing β -phenyl- $\alpha\alpha$ -dialkylpropionamides.

Phenyl *n*-propyl ketone, when treated first with sodamide in anhydrous ether and subsequently with benzyl chloride, gives a mixture of phenyl α -benzylpropyl ketone, $\text{COPh}\cdot\text{CHEt}\cdot\text{CH}_2\text{Ph}$, b. p. $183\text{--}184^\circ/13$ mm., giving an oxime, m. p. 78° ; and phenyl $\alpha\alpha$ -dibenzylpropyl ketone, $\text{COPh}\cdot\text{CET}(\text{CH}_2\text{Ph})_2$, m. p. $67\text{--}68^\circ$; b. p. $258^\circ/13$ mm. The former, when treated with sodamide in benzene and then with ethyl iodide, yields phenyl α -benzyl- α -ethylpropyl ketone, $\text{COPh}\cdot\text{CET}_2\cdot\text{CH}_2\text{Ph}$, m. p. $80\text{--}80.5^\circ$; b. p. $190\text{--}202^\circ/12\text{--}13$ mm., which can also be prepared by the benzylation of phenyl α -ethylpropyl ketone. Phenyl α -benzyl- α -ethylpropyl ketone reacts with sodamide to give α -benzyl- α -ethylbutyramide, which was not isolated in the free state, but was converted into α -benzyl- α -ethylbutyric acid, $\text{CH}_2\text{Ph}\cdot\text{CET}_2\cdot\text{CO}_2\text{H}$, b. p. $197\text{--}199^\circ/17$ mm., giving an acid chloride, b. p. $148^\circ/13$ mm. The acid chloride, in the presence of aluminium chloride in the cold, yielded 2:2-diethylindan-1-one, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix}\rangle\text{CET}_2$, m. p. 9° ; b. p. $138^\circ/13$ mm.

W. G.

Position of the Double Linking in Piperitone. I. A. R. PENFOLD (*Perf. Essent. Oil Rec.*, 1922, 13, 19—20).—Piperitone gave on oxidation with cold permanganate a product from which diosphenol was isolated, and identified by its reaction as a keto-phenol and by the preparation of the oxime and the phenylurethane. It is probable therefore that the double bond occupies the same position in piperitone as in diosphenol, and the former substance would accordingly be Δ^1 -menthen-3-one. G. F. M.

Constitution of Quinonoid Organic Onium Salts. F. KEHRMANN (*Helv. Chim. Acta*, 1922, 5, 69—71).—The recent criticisms of Hantzsch (this vol., i, 24) has led the author to state specifically that his formulæ (cf. A., 1918, i, 312; 1921, ii, 476) are applicable to carbonium salts. Further consideration, however, shows that it is unnecessary to indicate the particular union of the dissociable ion with the nitrogen atom, or, more generally, the basic point of attachment of the molecule by means of the dotted line as previously proposed. Nevertheless, it is advisable in writing the formulæ that the connexion between the dissociable ion and the basic group should be rendered sufficiently obvious either by placing them in close proximity or by marking the central atom in some particular manner, for example, by thickened type.

H. W.

Preparation of Intermediates [3-Chloro-2-aminoanthraquinone and 3-Chloro-1-bromo-2-aminoanthraquinone] and a Dyestuff of the Anthraquinone Series. FREDERICK WILLIAM ATTACK and CHARLES WILLIAM SOUTAR (Brit. Pat. 172682).—3-Chloro-2-aminoanthraquinone is obtained by the regulated chlorination at ordinary temperatures of 2-aminoanthraquinone in a suitable solvent such as glacial acetic acid or nitrobenzene until

the requisite increase in weight has taken place. It crystallises from acetic acid in orange-yellow needles, m. p. 221°. When 20 parts of the chloro-compound suspended with 10 parts of sodium carbonate in nitrobenzene are brominated at ordinary temperatures with 21 parts of bromine in 60 parts of nitrobenzene, 3-chloro-1-bromo-2-aminoanthraquinone is obtained as orange-coloured needles, m. p. 235°. This compound undergoes condensation on boiling in nitrobenzene solution with sodium and copper acetates with formation of a dyestuff having probably the constitution 3:3'-dichloroanthraquinone-1:2:1':2'-dihydroazine, but possibly the azine, as distinguished from the hydroazine, may be present. It dyes cotton bright blue shades from a hyposulphite vat. All the above reactions may be performed consecutively in the same liquid medium, for example, nitrobenzene, without isolation of the intermediate products. G. F. M.

Production of Dyestuff Intermediates [Aminoanthraquinones]. JOHN THOMAS, ARTHUR HUGH DAVIES, and SCOTTISH DYES, LTD. (Brit. Pat. 173006).—Higher yields of the corresponding aminoanthraquinones and products of better quality are obtained by heating 1-chloroanthraquinone or dichloroanthraquinones with aqueous ammonia in an autoclave than by the usual process with the sulphonic acids. The presence of small amounts of copper salts has a favourable influence on the course of the reaction. For example, a nearly theoretical yield of 1-aminoanthraquinone is obtained by heating 100 parts of 1-chloroanthraquinone with 700 parts of 26% ammonia at 170° for twelve hours in presence of 0.1 part of copper sulphate. G. F. M.

Preparation of 1-Chloro-2-aminoanthraquinone. ALEXANDER WALKER FYFE and BRITISH DYESTUFFS CORPORATION, LTD. (Brit. Pat. 173166).—1-Chloro-2-aminoanthraquinone is prepared, without previously protecting the amino-group by acetylation, by the direct chlorination at 15° of 2-aminoanthraquinone suspended in ten times its weight of nitrobenzene or other suitable solvent, such as acetic acid or chlorobenzene, until the requisite increase in weight has taken place. The yield amounts to 88% of the theoretical. G. F. M.

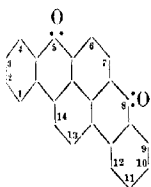
Some Products of the Reduction of 2-Hydroxyanthraquinone. ARTHUR GEORGE PERKIN and THOMAS WILLIAM WHATTAM (T., 1922, 121, 289—300).

Derivatives of β -Methylantraquinone. I. Syntheses of Chrysophanic Acid [1:8-Dihydroxy-3-methylantraquinone] and of 1:5-Dihydroxy-3-methylantraquinone. R. EDER and C. WIDMER (*Helv. Chim. Acta*, 1922, 5, 3—17).—The course of the reaction between α -nitrophthalic anhydride and *m*-cresol depends considerably on the condensing agent employed. In the presence of boric acid at 170—180°, 3'-(or 6')-nitro-3:6-dimethylfluoran, colourless, lustrous plates, m. p. 240—241°, a substance,

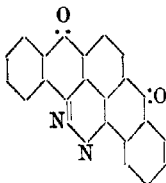
$C_{23}H_{19}O_6$, colourless needles, m. p. 210—211° (the constitution of which has not been elucidated), 6-nitro-o-2'-hydroxytoluoylbenzoic acid, $OH \cdot C_6H_3Me \cdot CO \cdot C_6H_3(NO_2) \cdot CO_2H$, coarse, pale green prisms, m. p. 227°, and 3-nitro-o-2'-hydroxy-p-toluoylbenzoic acid, prisms and needles, m. p. 239—240°, are formed. Attempts to convert the nitro-acids smoothly into anthraquinone derivatives by means of concentrated sulphuric acid were unsuccessful. In the presence of aluminium chloride, x-nitrophthalic anhydride and m-cresol give 3-nitro-o-2'-hydroxytoluoylbenzoic acid as the sole isolable product. The isomeric nitro-acids are reduced by ferrous hydroxide in boiling ammoniacal solution to 6-amino-o-2'-p-hydroxytoluoylbenzoic acid, almost colourless leaflets, m. p. 227—228°, and 3-amino-o-2'-hydroxytoluoylbenzoic acid, leaflets, m. p. 233—234°, respectively, which are converted in the usual manner into 6-hydroxy-o-2'-hydroxy-p-toluoylbenzoic acid, colourless, slender needles, m. p. 175—176°, and 3-hydroxy-o-2'-hydroxy-p-toluoylbenzoic acid, coarse, colourless needles, m. p. 229—230°. The 6-hydroxy-acid is transformed by concentrated sulphuric acid at 160—170° into 1:5-dihydroxy-3-methylanthraquinone, golden-yellow leaflets, m. p. 190—191°, whereas the 3-hydroxy-acid is converted by a mixture of boric and sulphuric acids into 1:8-dihydroxy-3-methylanthraquinone, yellow leaflets, m. p. 193—194°, which is identical in all respects with natural chrysophanic acid.

H. W.

Elimination of Hydrogen from Aromatic Nuclei, and Union of the Latter by means of Aluminium Chloride. IV. Ring Closure with Doubly Benzoylated Naphthalenes. ROLAND SCHOELL and HEINRICH NEUMANN (*Ber.*, 1922, 55, [B], 118—126; cf. A., 1913, i, 56, 734, and this vol., i, 258).—1:4-Dibenzoylnaphthalene is convertible into dibenzopyrene-5:8-quinone (annexed formula), but the corresponding compound from 1:5-dibenzoylnaphthalene could not be prepared.



1:4-Dicyanonaphthalene, long, pale yellow needles, m. p. 206°, is prepared by distilling sodium naphthalene-1:4-disulphonate with potassium cyanide and is hydrolysed by boiling, moderately concentrated sulphuric acid to naphthalene-1:4-dicarboxylic acid, m. p. 309°. The latter is converted by phosphorus pentachloride into naphthalene-1:4-dicarboxyl chloride, slender needles, m. p. 80°, which is transformed by benzene and aluminium chloride in the presence of carbon disulphide into 1:4-dibenzoylnaphthalene, colourless needles, m. p. 106°. The ketone yields, after treatment with aluminium chloride at 130°, a small amount of dibenzopyrene-5:8-quinone, broad, reddish-brown needles, m. p. 365°, which is purified preferably by sublimation. The corresponding dibenzopyrene, greenish-yellow leaflets or prisms, m. p. 281.5—282°, is formed by reduction of the quinone with zinc dust in an atmosphere of hydrogen. The quinone is oxidised by chromic acid



to 1:2-phthalylanthraquinone, yellow leaflets, m. p. 325°, which is transformed by hydrazine hydrate into the *azine* (annexed formula), orange-red needles, decomp. about 440°, after darkening at 430° in an atmosphere of hydrogen.

1:5-Dicyanonaphthalene, m. p. 260°, is converted successively into the corresponding dicarboxylic acid, m. p. 315–320° (decomp.), and its chloride; 1:5-dibenzoylnaphthalene, colourless crystals, m. p. 185–186°, is obtained from the latter. H. W.

Phenolcamphorcin. SRI KRISHNA (T., 1922, 121, 253–255).

Preparation of Terpeneol. ROBERT MARCHAND (Brit. Pat. 153605).—Terpeneol is obtained from terpin hydrate in nearly theoretical yield by distilling it with water and an organic sulphonic acid, preferably quinoline-8-sulphonic acid. The process may, if desired, be rendered continuous by adding further quantities of terpin hydrate as the terpeneol distils over. G. F. M.

The Main Constituent of Japanese Lac. VIII. Position of the Double Bonds in the Side Chain of Urushiol and Demonstration that Urushiol is not Homogeneous. RIKO MAJIMA (*Ber.*, 1922, 55, [B], 172–191; cf. A., 1920, i, 837, and previous abstracts).—Hydrourushiol is present to the extent of 10% in urushiol, the main constituent of Japanese lac. In addition, the following compounds are probably present: $C_6H_3(OH)_2[CH_2]_7CH:CH[CH_2]_5CH_3$, which on oxidation gives rise to heptaldehyde and the acid, $C_6H_3(OH)_2[CH_2]_7CO_2H$, or its homologues and $C_6H_3(OH)_2[CH_2]_7CH:CH[CH_2]_4CH:CH_2$, which yields, on oxidation, formic acid and the same aromatic substances as the preceding compound. The results of the analyses of the bromide and ozonide of the dimethyl ether and the volume of hydrogen absorbed during reduction indicate that it contains two double bonds in the molecule.

Urushiol is a mixture of compounds which differ from one another in the number and position of the double bonds present in the long, normal carbon chain. In this respect it exhibits a close similarity to the drying oils. It is difficult or almost impossible by the available methods to separate urushiol quantitatively into its components. Since, however, all the latter are converted by reduction into the same hydrourushiol, it appears desirable to retain the name urushiol for the original mixture, which is regarded as having a mean molecular formula, $C_{21}H_{32}O_2$ or $C_6H_3(OH)_2C_{15}H_{27}$. The isolation of veratrol-*o*-carboxylic acid from the products of the oxidation of urushiol dimethyl ether by potassium permanganate affords valuable confirmation of the constitution of urushiol as deduced by other methods.

[With YOSHIHIDE TAHARA.]—Diacetylurushiol is conveniently prepared by acetylating crude urushiol and distilling the product in a high vacuum (b. p. 212–220°/0.3 mm.). It is ozonised in

chloroform solution and the crude ozonide is decomposed with steam. The volatile products contain acetaldehyde, heptaldehyde, and *n*-heptoic acid; the non-volatile portions consist of diacetylhydrourushiol, 2:3-diacetoxyphenyl-*n*-octaldehyde, a pale yellow liquid, b. p. 205–207°/1 mm., and azelaic acid.

[With GITARO TAKAYAMA.]—Acetylhydrourushiol is converted into its *dioxonide*, and the latter is decomposed with steam. The products, isolated in the usual manner, are heptaldehyde, 2-acetoxy-3-methoxyphenyl-*n*-octaldehyde, $C_6H_5(OMe)(OAc)[CH_2]_7CHO$, b. p. 190–210°/0.8 mm., and the corresponding acid, which could not be caused to crystallise and is characterised by conversion into 2-hydroxy-3-methoxyphenyloctioic acid, colourless needles, m. p. 49–50°. The presence of acetylhydrourushiol monomethyl ether is also established.

[With WATANABE.]—Urushiol dimethyl ether is emulsified with water by the aid of a little palmitic acid and sodium hydroxide and oxidised with aqueous potassium permanganate solution initially at the atmospheric temperature and finally at 60°, whereby a mixture of salts and an oil is obtained. The latter contains hydrourushiol dimethyl ether. The mixture of salts is decomposed by sulphuric acid, yielding carbon dioxide, formic acid, oxalic acid, adipic acid, sebacic acid, veratrol-*o*-carboxylic acid, 2:3-dimethoxyphenyl-*n*-octoic acid, and its higher homologues.

[With WATANABE.]—Acetaldehyde has been isolated from the products of the decomposition of the ozonides of dimethylurushiol and diacetylurushiol, but not from that of urushiol monomethyl ether. The difference in behaviour is probably due to the more careful fractional distillation of the latter. A series of experiments with various fractions obtained from urushiol dimethyl ether indicates that the parent substance of the acetaldehyde accumulates in the fractions of lower boiling point, and demonstrates that urushiol is a mixture of closely allied substances which can only be separated from one another with difficulty by fractional distillation.

[With TAKAYAMA.]—The distillation of large quantities of urushiol monomethyl and dimethyl ethers has disclosed the presence of small amounts of an unsaturated volatile hydrocarbon to which the name *urusene* is applied: analyses indicate that it is probably a mixture of $C_{15}H_{28}$ and $C_{15}H_{26}$.

[With OKAZAKI.]—Urushiol dimethyl ether absorbs approximately four atomic proportions of bromine in carbon disulphide solution; the product obtained is not homogeneous. H. W.

The Chief Constituent of Japanese Lac. IX. Chemical Investigation of the different, naturally-occurring Species of Lac which are closely allied to Japanese Lac. RIKO MAJIMA (*Ber.*, 1922, 55, [B], 191–214; cf. preceding abstract).—A Burmese lac (from the stems of *Melanorrhæa usitata*, Wall), to which the name "Thitsi" is applied, is shown to contain thitsiol, a homologue of isohydrourushiol with an unsaturated side chain. As judged by the amount of hydrothitsiol formed by

reduction, however, this substance cannot comprise more than the third part of the material investigated. In this respect, the Burmese variety differs markedly from the Japanese and Indo-Chinese products, since in the latter cases the crude material consists of substances which are reducible to hydrourushiol or hydro-laccol to an extent of at least 90%. Indo-Chinese lac, probably tapped from *Rhus succedanea*, L., contains mainly laccol, which is reduced readily to hydro-laccol; the latter is isomeric with hydrothitsiol, and is a higher homologue of hydrourushiol. Formosa lac from *Semeocarpus vernicifera* and a product from *Rhus ambigua*, Lav., or *Rhus orientalis*, Schn, are shown to contain laccol as main constituent, whereas two specimens of Chinese lac (probably from *Rhus vernicifera* or a closely allied species) contained mainly urushiol. A Siamese lac was found to be impure and to consist in all probability of a mixture of Indo-Chinese and Burmese lac.

[With CHOZO CHIBA.]—The Indo-Chinese lac is purified by solution in alcohol, filtration, and evaporation of the filtrate, treatment of the residue with saturated aqueous sodium chloride solution, and, finally, with light petroleum. It is thus obtained as a pale-brown, viscous liquid which resembles urushiol closely in appearance and in chemical behaviour. When treated with methyl iodide and sodium ethoxide, it is transformed into laccol dimethyl ether, $C_6H_3(OMe)_2C_{17}H_{31}$, b. p. $206-208^\circ/0.25$ mm., $d_{20}^{25} 0.92954$. It is reduced by hydrogen in the presence of platinum black to hydro-laccol, $C_6H_3(OH)_2C_{17}H_{35}$, m. p. $63-64^\circ$, which is oxidised by potassium permanganate in the presence of acetone to stearic acid. *Hydro-laccol dimethyl ether*, obtained by the catalytic hydrogenation of laccol dimethyl ether, crystallises in long prisms, m. p. $43-44^\circ$; with nitric acid it yields 5-nitrohydro-laccol dimethyl ether, m. p. $75-76^\circ$, and 5:6-dinitrohydro-laccol dimethyl ether, m. p. $86-87^\circ$.

[With YOSHIHIRO KUDO.]—A solution of laccol dimethyl ether in chloroform is converted by ozone into a *mono-ozonide*. The latter is decomposed by boiling water into heptaldehyde, acetaldehyde, formic acid, oxalic acid, an impure aldehyde of the composition $C_6H_3(OMe)_2[CH_2]_9\cdot CHO$, and nonane- ω : ω' -dicarboxylic acid, m. p. $109-111^\circ$.

Hydro-laccol is shown to be contained in the crude laccol, thus giving an analogy to the occurrence of hydrourushiol in urushiol (preceding abstract).

[With CHOZO CHIBA.]—The isolation of thitsiol from the black variety of "Thitsi" or Burmese lac is effected by means of alcohol and light petroleum. *Thitsiol dimethyl ether*, $C_{25}H_{40}O_2$, is a pale yellow, viscous liquid, b. p. $204-205^\circ/0.2$ mm., $d_{20}^{25} 0.96390$. *Hydro-thitsiol*, $C_6H_3(OH)_2C_{17}H_{35}$, has m. p. $94-96^\circ$. *Hydrothitsiol dimethyl ether* crystallises in leaflets, m. p. $56-57^\circ$; it is transformed by nitric acid in glacial acetic acid solution into 6-nitrohydrothitsiol dimethyl ether, pale yellow needles, m. p. $75-76^\circ$. Hydrothitsiol is shown to be identical with heptadecylcatechol by the direct synthesis of the latter; for this purpose, margaric acid is condensed with catechol in the presence of tin chloride and the

3:4-dihydroxyphenyl hexadecyl ketone, m. p. 100—103°, thus formed is reduced by Clemmensen's method to heptadecylcatechol.

The proximity to fresh lac juice or even to the lac tree is known to produce a painful but not dangerous skin disease in susceptible persons; this is now shown to be caused by urushiol, and is produced in order of decreasing intensity by distilled urushiol, ordinary urushiol, and crude Japanese lac. Similar effects are produced by other urushiol derivatives, and in this respect urushiol, hydro-urushiol, urushiol dimethyl ether, and hydrourushiol dimethyl ether are placed in order of diminishing activity. The action of urushiol is attributed to the conjoint effect of two contiguous hydroxyl groups and the unsaturated alkyl radicle. A series of experiments with catechol derivatives shows that the intensity of the action increases with increasing length of the alkyl chain, but is not noticeably affected by its position. Laccol of Indo-Chinese, Formosa, and Tsutaurnshi lac is approximately as toxic as thitsiol of Burmah lac, but either substance attacks the skin much less violently than urushiol of Japanese or Chinese lac.

H. W.

Kawa-kawa Resin. YOSHIIHARU MURAYAMA and KENJIRO MAYEDA (*J. Pharm. Soc. Japan*), 1921, No. 477, 959—968.—S. Murakami (*ibid.*, 1916, 393, and 1918, 563) isolated three compounds: demethoxy-yanoquinone, $C_{14}H_{12}O_3$, m. p. 133—134°, β -methylstearic acid, $C_{14}H_{24}O_2$, m. p. 175°, and kawaic acid, $C_{14}H_{18}O_4$ or $C_{14}H_{16}O_6$, m. p. 84—86°, from the kawa-kawa resin. The authors investigated kawaic acid and found that it corresponds with the empirical formula $C_{15}H_{16}O_5$, and contains one methoxyl group. When heated with alcoholic potash, it gives benzaldehyde and a compound, $C_{14}H_{16}O_3$, light yellow leaves, m. p. 164° (decomp.), which contains one methoxyl group. By oxidation with 2% potassium permanganate, it yields benzaldehyde and benzoic acid. From the mother-liquor from which kawaic acid was isolated a new acid, β -kawaic acid, $C_{14}H_{18}O_4$, colourless, slender needles, m. p. 101—103°, was isolated; it is moderately soluble in boiling water and ether, and very soluble in alcohol. It contains a methoxyl group and yields benzoic acid when oxidised with 5% potassium permanganate.

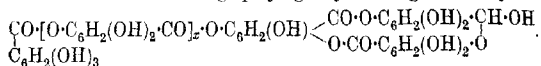
K. K.

The Tinctorial Properties of some Anthocyanins and certain Related Pigments. II. ARTHUR E. EVEREST and ARCHIBALD JOHN HALL (*J. Soc. Dyers and Col.*, 1922, **38**, 9—13; cf. A., 1921, i, 485).—An account of experiments carried out with a view to study the influence on the tinctorial properties of the introduction of acidic and basic radicles in the benzene nucleus of synthetic pigments related to anthocyanins.

Attempts to prepare amino-derivatives by nitration and reduction failed, for treatment of 2-phenylbenzopyroniumferriehloride with nitric acid, or nitric acid and sulphuric acid, resulted in oxidation, but satisfactory results were obtained by an indirect method. Diazotised amines, such as aniline, o- and p-toluidine,

sulphanilic acid, *p*-nitroaniline, α - and β -naphthylamine, couple with phenyl *o*-hydroxystyryl ketone, probably in the *p*-position with respect to the hydroxyl group, and on reduction yield an amino-derivative which is converted into the corresponding oxonium salt by alcoholic hydrochloric acid. The azo-compounds which were prepared from phenyl *o*-hydroxystyryl ketone possess an affinity for wool, but owing to their sparing solubility in water, their application is difficult, except in the case of the compound derived from sulphanilic acid. The corresponding azo-pyrylium compounds are to be dealt with subsequently. F. M. R.

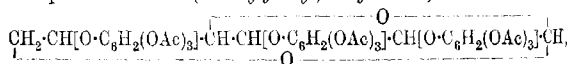
Gallotannin. M. NIERENSTEIN (*J. Soc. Chem. Ind.*, 1922, 41, 29—30t; cf. Nierenstein, Spiers, and Geake, T., 1921, 119, 275).—A critical discussion of the attempts to elucidate the constitution of gallotannin is given. It is considered that it is probably a glucoside of the following polydigalloylleucodigallic anhydride,



The formula explains the high molecular weight, the optical activity, and the low electrical conductivity of gallotannin. It is in accord with the observation that gallotannin is more acidic than pyrogallol towards diazoacetic ester. It accounts for the mutarotation of gallotannin and explains the different phases observed in the formation of ellagic acid from gallotannin. It is in accordance with the formation of tetramethylglucose from methylgallotannin. None of the four points last mentioned is explicable on the basis of Fischer's conception of gallotannin as pentadigalloylglucose.

H. W.

Crystalline Synthetic Tannins. I. P. KARRER and HARRY R. SALOMON (*Helv. Chim. Acta*, 1922, 5, 108—123).—A solution of laevoglucosan in chloroform is converted by triacetylalloyl chloride and quinoline into *tri-(triacetylalloyl)laevoglucosan*,



m. p. (indefinite) 137°, after softening at 126°, $[\alpha]_D^{25}$ —10.45°, in acetone solution, which has not been obtained in the crystalline condition. It is hydrolysed by an excess of sodium hydroxide in aqueous acetone solution at 0° and the solution, after neutralisation and removal of acetone in a vacuum, deposits successively two gelatinous precipitates (*A* and *B*) when preserved. The former dissolves freely in cold alcohol, but by allowing the alcoholic solution to evaporate slowly at the atmospheric temperature it gradually becomes crystalline and sparingly soluble in alcohol. It is subsequently readily crystallised from this solvent, and yields α -*trigalloyl)laevoglucosan*, long, six-sided crystals, decomp. 250—320°, $[\alpha]_D^{25}$ —18.02° in alcoholic solution. The ability of the substance (and others of this class) to give the typical tannin reactions cannot be investigated, since it is insoluble in water, but in 10% alcoholic

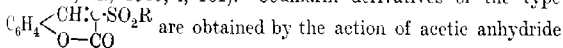
solution it readily causes gelatinisation with arsenic acid. It gives a *potassium* salt which is sparingly soluble in alcohol. The precipitate, *B* (see above), yields β -*trigalloyllævoglucozan*, broad needles, and flat, rectangular plates, decomp. $270-320^\circ$, $[\alpha]_D^{25} -21.00^\circ$ in alcoholic solution (the *potassium* salt is described). The α - and β -compounds are differentiated clearly by their behaviour towards ferric chloride in alcoholic solution, since the former gives a bluish-black, gelatinous precipitate, whereas, under similar conditions, the latter gives only a bluish-violet solution without a precipitate. *Digalloyllævoglucozan*, colourless needles, decomp. $220-270^\circ$, $[\alpha]_D^{18} -27.93^\circ$ in alcoholic solution, is prepared by extraction of the filtrate from the precipitates *A* and *B* with ethyl acetate, removal of the solvent, and treatment of the residue with aqueous acetone; the sparingly soluble *potassium* salt is described. The mother-liquors from the crystallisation of the digalloyl derivative contain gallic acid and *monogalloyllævoglucozan*, decomp. 240° after darkening at 220° .

It is remarkable that the trigalloyllævoglucozans, when impure, are freely soluble in acetone or alcohol, in which they dissolve but sparingly after being recrystallised; similarly, crude digalloyllævoglucozan dissolves with great ease in water, whereas the pure product is very sparingly soluble. It appears probable, therefore, that the natural and synthetic tannins which are freely soluble in water and alcohol are all mixtures the components of which in the pure condition are characterised by sparing solubility.

The typical tannin reactions, such as the gelatinisation of alcoholic arsenic acid solution, are not exhibited by monogalloyllævoglucozan, which in this respect behaves similarly to Fischer's monogalloylglucose; the presence of at least two galloyl residues in the sugar molecule appears essential to the development of tannin characteristics.

H. W.

Synthesis of α -Benzopyrone Derivatives and the Rupture of the Pyrone Ring in these Compounds. J. TRÖGER and FR. BOLTE (*J. pr. Chem.*, 1921, [ii], **103**, 163-187; cf. Tröger and Lux, A., 1910, i, 161).—Coumarin derivatives of the type



are obtained by the action of acetic anhydride at water-bath temperature on a mixture of salicylaldehyde and the requisite arylsulphonylacetic acid. From benzenesulphonylacetic acid is obtained 3-benzenesulphonylcoumarin, m. p. $217-217.5^\circ$ (*loc. cit.*), from *p*-toluenesulphonylacetic acid, 3-*p*-toluenesulphonylcoumarin, colourless, tabular crystals, m. p. 221° , and from *p*-chlorobenzenesulphonylacetic acid, 3-*p*-chlorobenzenesulphonylcoumarin, m. p. 242° (*loc. cit.*). 3-Benzenesulphonylcoumarin is changed by alcoholic sodium ethoxide at water-bath temperature into *phenyl-o*-hydroxystyrylsulphone, $OH \cdot C_6H_4 \cdot CH : CH \cdot SO_2 \cdot C_6H_5$, colourless plates, m. p. 166° ; the corresponding *acetoxy*-compound has m. p. 123° and the *benzoyloxy*-derivative, m. p. 135° . The following compounds were prepared in similar manner. *p*-Tolyl-*o*-hydroxystyrylsulphone, $OH \cdot C_6H_4 \cdot CH : CH \cdot SO_2 \cdot C_6H_4Me$, colourless

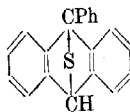
plates, m. p. 154°; the *acetoxy*-derivative, m. p. 109°; and *benzoyloxy*-derivative, m. p. 98°; *p*-chlorophenyl-*o*-hydroxystyrylsulphone, m. p. 168—169°; *acetoxy*-derivative, m. p. 126°; and *benzoyloxy*-derivative, m. p. 96°.

Benzenesulphonylacetic acid and resorcyaldehyde (CHO:OH:OH = 1 : 2 : 4) with acetic anhydride gives 7-*acetoxy*-3-benzenesulphonylcoumarin, colourless needles, m. p. 237°, but only if there be some sodium benzenesulphonylacetate in the free acid. With sulphuric acid, 7-*acetoxy*-3-benzenesulphonocoumarin yields 7-*hydroxy*-3-benzenesulphonylcoumarin. On alkaline hydrolysis, the acetyl compound yields phenyl-2 : 4-dihydroxystyrylsulphone, $C_6H_3(OH)_2 \cdot CH:CH \cdot SO_2Ph$, yellow crystals, m. p. 209—210°, of which the following derivatives are described: *dimethyl ether*, a pale yellow powder, m. p. 108°; *diacetoxy*-derivative, leafy crystals, m. p. 112°; *dibenzoyloxy*-derivative, colourless needles, m. p. 77°. Similarly, 7-*acetoxy*-3-*p*-toluenesulphonylcoumarin, m. p. 234°; 7-*hydroxy*-3-*p*-toluenesulphonylcoumarin, m. p. 239°; *tolyl*-2 : 4-dihydroxystyrylsulphone, m. p. 184°; and its *dimethyl ester*, m. p. 108°; *dinacetoxy*-derivative, m. p. 108°; and *dibenzoyloxy*-derivative, m. p. 132°, and 7-*acetoxy*-3-*p*-chlorobenzenesulphonylcoumarin, rhombic crystals, m. p. 224°; 7-*hydroxy*-3-*p*-chlorobenzenesulphonylcoumarin, small, transparent needles, m. p. 226°; *p*-chlorophenyl-2 : 4-dihydroxystyrylsulphone, transparent crystals, m. p. 193°, and its *dimethyl ether*, m. p. 77°; *diacetoxy*-derivative, m. p. 112°; *dibenzoyloxy*-derivative, m. p. 164°, were prepared. No derivatives of coumarinic or coumaric acid could be isolated on attempting to rupture the pyrone ring, but they are to be assumed as intermediate stages in some of the hydrolyses.

W. O. K.

Sulphur as the Bridge Atom in the Middle Ring of a Derivative of Anthracene. A. BISTRZYCKI and B. BRENNEN

(*Helv. Chim. Acta*, 1922, 5, 20—28; cf. A., 1915, i, 245; 1920, i, 629).—The action of concentrated sulphuric acid on 2 : 4 : 4-triphenyl-1 : 3-oxthiophan-5-one, $CPh_2 \begin{smallmatrix} \diagup S \diagdown \\ \diagdown CO \diagup \end{smallmatrix} CHPh$, has been ex-



amined further and is shown to yield 9-phenyl-9 : 10-dihydromesothioanthracene.

2 : 4 : 4-Triphenyl-1 : 3-oxthiophan-5-one dissolves gradually in sulphuric acid (*d* 1.84) with brisk evolution of carbon monoxide and formation of a yellow solution which rapidly becomes dark violet-red. The solution is neutralised with aqueous ammonia and boiled until the precipitate becomes flocculent, thus yielding 9-phenyl-9 : 10-dihydromesothioanthracene, slender, yellow needles, m. p. 117—118°. The latter is converted by distillation with zinc dust into 9-phenylanthracene, m. p. 152°, the production of which suggests the possibility that the parent substance is in reality the thioketone, $C_6H_4 \begin{smallmatrix} \diagup CHPh \\ \diagdown CS \end{smallmatrix} \diagup C_6H_4$. This hypothesis, however, is negated by its stability towards phenylhydrazine alcoholic sodium hydroxide solution, and aniline, as well as by

its reduction by zinc and hydrochloric acid in the presence of glacial acetic acid to 1:3-diphenylthiophthalan, $\text{C}_6\text{H}_5\text{C}(\text{CHPh})_2\text{S}$, colourless, silky needles, m. p. 106.5–107.5°, the constitution of which follows from its conversion by more drastic treatment with the same reagents into *o*-dibenzylbenzene, m. p. 78°. Oxidation of phenyldihydromesothioanthracene with hydrogen peroxide in glacial acetic acid solution gives *o*-dibenzoylbenzene, m. p. 145–146°, which is shown by direct comparison to be identical with the product prepared by Simonis and R Emmert (A., 1915, i, 136).

4:4-Diphenyl-2-*p*-chlorophenyl-1:3-oxthiophan-5-one (A., 1920, i, 631) is similarly converted by sulphuric acid into 2-chloro-9-phenyl-9:10-dihydromesothioanthracene, microscopic aggregates of yellow prisms, m. p. 124–126° after softening at 120°. H. W.

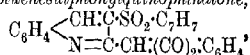
Constitution of Matrine. II. HEIZABURŌ KONDŌ, NICHIRŌ KISHI, and CHŪRŌ ARAKI (*J. Pharm. Soc. Japan*, 1921, 1047–1069; cf. A., 1921, i, 882).—By reducing matrine with sodium and amyl alcohol, *deoxymatrine*, $(\text{C}_{15}\text{H}_{24}\text{N}_2)_2$, rhombic prisms, m. p. 162° (*aurichloride*, yellow, amorphous precipitate; *platinichloride*, orange-yellow plates, decomposes at 284°. The *dimethiodide*, colourless needles, m. p. 178°, and its *aurichloride*, yellow needles, m. p. 180°; *platinichloride*, an orange-yellow, crystalline precipitates, decomposing at 282°; *picrate*, yellow, slender crystals, m. p. 109°; *mercurichloride*, white prisms, m. p. 175–180°), and *deoxymatrine oxide*, $(\text{C}_{15}\text{H}_{24}\text{N}_2)_2\text{O}$, a yellow, amorphous base, were obtained. To reduce the products further, *deoxymatrine* was heated with hydrogen iodide (*d* 1.7) and red phosphorus at above 250° for five hours, when *dimatridine*, $(\text{C}_{15}\text{H}_{25}\text{N}_2)_2$, long, colourless needles, m. p. 160° (*platinichloride*, orange-yellow needles, decomposing at 275°; *aurichloride*, yellow needles, m. p. 215°; *dimethiodide*, an amorphous precipitate; and its *aurichloride*, a yellow, crystalline powder, decomposing at 193°; *platinichloride*, a light reddish-yellow, crystalline powder, decomposing at 279°; *mercurichloride*, a white powder, m. p. about 150°; *picrate*, a yellow powder, m. p. about 92°), and a crystalline base, m. p. 75–76°, isomeric with the former, were produced. *Dimatridine* was formed also by the catalytic reduction of *deoxymatrine* with hydrogen in the presence of platinum black. *Deoxymatrine oxide*, when subjected to reduction with hydrogen iodide and red phosphorus, yielded the base, $\text{C}_{16}\text{H}_{16}\text{N}$, described in the former paper. The electrolytic reduction of matrine did not give a satisfactory result, but a small quantity of an unsaponifiable crystalline base, m. p. 72–76°, was formed (*platinichloride*, decomposing at 254°, and *aurichloride*, m. p. 206–208°). K. K.

Synthesis of β -Arylsulphonylquinolines containing a Side Chain in the 2-Position. J. TRÜGER and W. MENZEL (*J. pr. Chem.*, 1921, [ii], 103, 188–215).—3-*p*-Toluenesulphonyl-2-methylquinoline, $\text{C}_6\text{H}_5\text{C}(\text{N}(\text{CH}_3)_2)\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$, obtained by heating an

alcoholic solution of *o*-aminobenzaldehyde with *p*-toluenesulphonyl acetone, and a small amount of sodium hydroxide, forms lustrous, broad needles, m. p. 152°, and on distillation with zinc dust yields 2-methylquinoline, thus proving its constitution. The following derivatives are described: *hydrochloride*, $C_{17}H_{15}O_2NS.HCl$, m. p. 150°; *nitrate*, m. p. 138°; *sulphate*, $C_{17}H_{15}O_2NS.H_2SO_4$; *oxalate*, $C_{17}H_{15}O_2NS.C_2O_4H_2$, decomp. 145°; *platinichloride*,

$(C_{17}H_{15}O_2NS)_2.H_2PtCl_6$, m. p. 216°; *aurichloride*, $C_{17}H_{15}O_2NS.HAuCl_4$, m. p. 194°; *mercurichloride*, m. p. 148°; *stannochloride*, $(C_{17}H_{15}O_2NS)_2.H_2SnCl_4$, m. p. 235°; *methiodide*, $C_{17}H_{15}NSO_2.MeI$, m. p. 146°; *methochloride*,

m. p. 156°; the *benzylidene* derivative, $C_6H_4 \begin{smallmatrix} \diagup CH:C\cdot SO_2\cdot C_6H_7 \\ \diagdown N=C\cdot CH:CH\cdot C_6H_5 \end{smallmatrix}$, yellowish-white needles, m. p. 204° (*hydrochloride*, m. p. 202°); the corresponding *ethylidene* derivative, m. p. 165° (*hydrochloride*, m. p. 160°), and β -*p*-toluenesulphonylquinophthalone,



small, brittle prisms, m. p. 147°.

In the same way, from benzenesulphonylacetone and *o*-aminobenzaldehyde is obtained 3-benzenesulphonyl-2-methylquinoline, yellowish-white, thin needles, m. p. 144°, and the following derivatives: *hydrochloride*, $C_{16}H_{13}O_2NS.HCl$, m. p. 105°; *nitrate*, m. p. 126°; *sulphate*, decomp. 150°; *oxalate*; *platinichloride*; *aurichloride*, m. p. 186° (decomp.); *mercurichloride*, m. p. 95°; *stannochloride*, m. p. 245°; *methiodide*, $C_{16}H_{13}O_2NS.CH_3I$, m. p. 135°; *methochloride*, m. p. 149°; the *benzylidene* derivative, $C_{22}H_{17}O_2NS$, slender needles, m. p. 195° (*hydrochloride*, m. p. 198°); the *ethylidene* derivative, $C_{18}H_{15}NSO_2$, small, nodular crystals, m. p. 154° (*hydrochloride*); and 3-benzenesulphonylquinophthalone, $C_{24}H_{19}O_2NS$, yellow needles, m. p. 140°. Similarly, from *p*-chlorobenzenesulphonylacetone is obtained 3-*p*-chlorobenzenesulphonyl-2-methylquinoline, lustrous, colourless, long, slender needles, m. p. 155°, and the following derivatives: *hydrochloride*, $C_{16}H_{12}O_2NSCl.HCl$, m. p. 200°; *nitrate*, m. p. 132°; *sulphate*, *oxalate*, *platinichloride*, *aurichloride*, m. p. 180°; *mercurichloride*, m. p. 195–198°; *stannochloride*, m. p. 235°; *methiodide*, $C_{16}H_{12}O_2NSCl.CH_3I$, m. p. 150°; *methochloride*, m. p. 160°; the *benzylidene* derivative, $C_{22}H_{15}O_2NSCl$, a yellowish-green, microcrystalline powder, m. p. 200° (*hydrochloride*); the *ethylidene* derivative, $C_{18}H_{14}O_2NSCl$, slender, yellowish-white needles, m. p. 185° (*hydrochloride*); and 3-*p*-chlorobenzenesulphonylquinophthalone, $C_{24}H_{17}O_2NSCl$, small, rhombic crystals, m. p. 150°. In no case could the benzylidene or ethylidene derivative be oxidised to the corresponding carboxylic acid.

From β -naphthalenesulphonylacetone and *o*-aminobenzaldehyde 3- β -naphthalenesulphonyl-2-methylquinoline, $C_6H_4 \begin{smallmatrix} \diagup C\cdot SO_2\cdot C_{10}H_7 \\ \diagdown N\cdot CMc \end{smallmatrix}$,

is obtained as greyish-white, prismatic needles, m. p. 160°; *platinichloride*, $(C_{26}H_{17}O_2NS)_2.H_2PtCl_6$, m. p. 228°. By using benzenesulphonylacetophenone derivatives, corresponding phenylquinolines are obtained and will be described later.

W. O. K.

Extension of the Kishner-Wolff Method of Reduction. I. ERNST THIELEPAPE (*Ber.*, 1922, 55, [B], 136—138).—The replacement of the oxygen atom of ketones and aldehydes by hydrogen has been effected by Wolff (A., 1912, i, 988) through the corresponding hydrazones. The extension of the reaction to carbonyl groups in general is now being investigated together with the decomposition of substituted hydrazine or hydrazone groups with the elimination of nitrogen in the cases of substances which are not derived from true ketones or aldehydes.

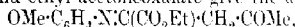
4-Methylquinoline-2-hydrazone, $C_6H_4 \begin{smallmatrix} < CMe:CH \\ NH-C:N \cdot NH_2 \end{smallmatrix}$, m. p. 148°,

is prepared from 2-chloro-4-methylquinoline, more conveniently from 4-methylquinoline and hydrazine hydrate. The hydrazone is converted into 4-methylquinoline when heated during seventy-two hours at 150—180° with potassium hydroxide, or by treatment of its solution in boiling water with copper sulphate or in cold water with iron chloride. H. W.

The Quinoline Series. I. Synthesis of 4-Substituted Quinolines and of Quinoline-4-carboxylic Acids. ERNST THIELEPAPE (*Ber.*, 1922, 55, [B], 127—135).—Attempts are described to synthesise 4-substituted quinolines or 2:4-disubstituted quinolines in which the substituent in position 2 is easily removable.

Aniline hydrochloride and sodium formylacetone yield the *anil*, $NPh:CH:CH_2:CO:CH_3$, colourless crystals, m. p. 91·5°; after being distilled in a high vacuum (b. p. 128—134°/2·5—5 mm.), the product has m. p. about 61° and then passes into the modification, m. p. 91·5°, which is also produced when attempts are made to crystallise the variety, m. p. 61°. The nature of the isomerism has not been elucidated. All attempts to effect ring closure with formation of a quinolyl derivative were unsuccessful.

p-Anisidine and ethyl acetoneoxalate give the *anil*,



yellow crystals, m. p. 68°, which could not be converted into a substituted quinoline.

α -Ethoxalyl-N-methylacetanilide, $NMePh \cdot CO \cdot CH_2 \cdot CO \cdot CO_2Et$, colourless crystals, m. p. 84·5°, is prepared by the condensation of N-methylacetanilide with ethyl oxalate in ethereal solution in the presence of sodium ethoxide. It is converted by concentrated sulphuric acid at -15° into ethyl 1-methyl-2-quinolone-4-carboxylate,

$C_6H_4 \begin{smallmatrix} < C(CO_2Et):CH \\ NMe-CO \end{smallmatrix}$, m. p. 134—135°, which is hydrolysed by

boiling aqueous sodium hydroxide to the corresponding acid, m. p. 251—252°. The ester is converted by phosphorus pentachloride in the presence of phosphoryl chloride into ethyl 2-chloroquinoline-4-carboxylate, yellow crystals, m. p. 64·5° (2-chloroquinoline-4-carboxylic acid may be obtained similarly from 2-hydroxyquinoline-4-carboxylic acid). 2-Hydrazinoquinoline-4-carboxylic acid, unstable, yellow crystals which do not melt below 305°, is obtained from the chloro acid and hydrazine; the corresponding

hydrazide, colourless, unstable crystals, m. p. 228–229° (decomp.) after darkening and softening above 190°, is prepared from ethyl 2-chloroquinoline-4-carboxylate. Quinoline-4-carboxylic ester is converted similarly into *quinoline-4-carboxyhydrazide*, colourless crystals, m. p. 154·5°. *2-Iodoquinoline-4-carboxylic acid*, almost colourless crystals, m. p. 195–196°, after darkening at 180° and softening at 190°, is prepared from the 2-chloro-acid by the action of potassium iodide and red phosphorus in the presence of hydriodic acid (*d* 1·50). H. W.

Arylated Pyridines. III. Quinodihydropyridines. W. DILTHEY (*Ber.*, 1922, 55, [B], 57–59; cf. A., 1920, i, 448; 1921, i, 735).—The pyridine analogues of the deeply coloured anhydrobases obtained by the action of dilute alkali on *p*-hydroxyarylpyrylium salts are readily prepared when the pyridine nitrogen atom is united to an aromatic residue. Thus 1:2:6-triphenyl-4-*p*-hydroxyphenylpyridinium chloride, pale yellow crystals which do not melt below 340° (obtained from 2:6-diphenyl-4-*p*-hydroxyphenylpyrylium chloride and aniline), is converted by ammonia in alcoholic solution into 1:2:6-triphenyl-4-quinopyridan, $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_5\text{NH}_2\text{Ph}_3$, yellowish-red needles, m. p. 302°. Solutions of the substance or its salts are not fluorescent. H. W.

New Method for the Preparation of Alkamines. II. JIRŌ TAKEDA and SAJŪRŌ KURODA (*J. Pharm. Soc. Japan*, 1921, 1—76).—The authors have shown (A., 1920, i, 228) that styrene dibromide, anethole dibromide, and the like reacting with carbamide produce substituted dihydro-oxazoles, which are changed to the corresponding alkamines by the action of alkali hydroxides. By the decomposition of the methyl derivatives of these dihydro-oxazoles, *N*-methylalkamines are, however, obtained, so that the imino-

oxazolidine formula, $\begin{array}{c} \text{R} \cdot \text{CH} \cdot \text{NH} \\ | \\ \text{R}' \cdot \text{CH} - \text{O} \end{array} > \text{C} \cdot \text{NH}$, must replace the

constitution, $\begin{array}{c} \text{R} \cdot \text{CH} \cdot \text{N} \\ | \\ \text{R}' \cdot \text{CH} - \text{O} \end{array} > \text{C} \cdot \text{NH}_2$, given earlier. By the action

of acetic anhydride and sodium acetate, these compounds are converted mainly into acetyl derivatives, $\begin{array}{c} \text{R} \cdot \text{CH} \cdot \text{N} \cdot \text{Ac} \\ | \\ \text{R}' \cdot \text{CH} - \text{O} \end{array} > \text{C} \cdot \text{NH} \cdot \text{CH}_3 \cdot \text{CO}_2\text{H}$,

but to a small extent into the acetyloxazolidones, $\begin{array}{c} \text{R} \cdot \text{CH} \cdot \text{N} \cdot \text{Ac} \\ | \\ \text{R}' \cdot \text{CH} - \text{O} \end{array} > \text{CO}$;

the hydrolysis of the former by alkali hydroxides produces the corresponding alkamine through the oxazolidone more easily than imino-oxazolidines themselves. In these reactions, an isomeric β -alkamine is produced in small quantity with the α -alkamine; the *isoadrenaline* base of Mannich (A., 1910, i, 411) corresponds with the former. The method was applied to dihydronaphthalene dibromide, which with carbamide yields the corresponding imino-oxazolidine; this is converted into the corresponding alkamine by way of the acetyl derivative. The bases are not identical with those described by Bamberger and Lodter (A., 1893, i, 591;

1896, i, 99), but are stereoisomerides. The following substances were prepared.

I. Anetholealkamine group. 4-*p*-Anisyl-5-methyloxazolidone, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NH}>\text{CO}$, rhombic plates, m. p. 110–112°, is

prepared by heating anethole-2-imino-oxazolidine with water at 140–150° in a sealed tube with a small quantity of anetholealkamine; *acetyl* derivative, hexagonal plates, m. p. 111–112°.

4-*p*-Anisyl-5-methyloxazoline mercaptan, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}>\text{CSH}$, $\text{Me}\cdot\text{CH}-\text{O}$

white plates, m. p. 86–88°, from anetholealkamine, carbon disulphide, and potassium hydroxide; *acetyl* derivative, colourless plates, m. p. 79–81°. α -*p*-Hydroxyphenyl- β -hydroxypropylamine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{NH}_2)\cdot\text{CHMe}\cdot\text{OH}$, colourless, hexagonal plates, m. p. 173°, from anetholealkamine and hydrogen iodide (*hydrochloride*, m. p. 187°; *dibenzate*, m. p. 173°), which yields α -*p*-hydroxyphenyl-methyl- β -hydroxypropylamine, with methyl iodide; *hydrochloride*, m. p. 184–186°. β -Anetholealkamine, thin plates, m. p. 80°, is prepared by heating anethole oxide with alcoholic ammonia at 130° (*copper salt*, m. p. 161°). By acetylation of the bromo-anethole-2-imino-oxazolidine with acetic anhydride and sodium acetate, its *N*-*acetyl* derivative, plates, m. p. 190–192°, and the *acetyloxazolidone*, m. p. 134°, are prepared; the former gives bromoanetholealkamine (α -*p*-methoxybromophenyl- β -hydroxypropylamine), thin plates, m. p. 118° (*hydrochloride*, m. p. 247°; *copper derivative*, m. p. 168°).

II. *isosafolealkamine* group. 4-Methylenedioxyphenyl-5-methyloxazolidone, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{NH}>\text{CO}$, plates, m. p. 170–171°, $\text{Me}\cdot\text{CH}-\text{O}$

is prepared by heating *isosafole*-2-imino-oxazolidine with water at 140° in a sealed tube, *isosafolealkamine* and ammonia being simultaneously formed. By acetylation of *isosafole*-2-imino-oxazolidine with acetic anhydride and sodium acetate, the *N*-*acetyl*-acetate, m. p. 208°, and the *acetyloxazolidone*, colourless prisms, m. p. 116–119°, are formed, the former, when heated at 205°, is changed first into the latter, and then into β -*isosafolealkamine* (*copper salt*, m. p. 171–173°). Benzoylation of *isosafole*-2-imino-oxazolidine by Schotten-Baumann's method yields only the *N*-benzyloxazolidone, m. p. 180–182°. When boiled with 30% sodium hydroxide, the *acetyl*-acetate yields *isosafolealkamine*, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CHMe}\cdot\text{OH}$, slender needles, m. p. 79° (*hydrochloride*, m. p. 210–215°; *platinichloride*, orange-yellow crystals, m. p. 200–202°; *copper derivative*, $(\text{C}_{10}\text{H}_{13}\text{O}_3\text{N})_2\text{CuO} + 2\text{H}_2\text{O}$, deep violet crystals, m. p. 185–186°), whilst with very dilute alkali the free *N*-*acetyl* derivative, m. p. 153°, is formed. By acetylation with acetic anhydride, *isosafolealkamine* gives the *N*-*acetyl* derivative, prisms, m. p. 136°, which change to *isosafolealkamine acetate* (*hydrochloride*, needles, m. p. 198–200°, when treated, in benzene suspension, with hydrogen chloride; *platinichloride*, orange-yellow crystals, m. p. 200°). In the same way,

N-benzoylisosafrolealkamine, needles, m. p. 139°, suffers rearrangement to isosafrolealkamine benzoate (hydrochloride, m. p. 203°; platinichloride, m. p. 201°). By heating with carbon disulphide and potassium hydroxide, isosafrolealkamine produces the mer. captan, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{N}\begin{smallmatrix} \diagup \\ \text{MeCH}\cdot\text{O} \end{smallmatrix}\text{C}\cdot\text{SH}$, granules, m. p. 160°; the

acetyl-mercaptan forms white, hexagonal plates, m. p. 93°. Methyl. isosafrole-2-imino-oxazolidine, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{NMe}\begin{smallmatrix} \diagup \\ \text{Me}\cdot\text{CH}\cdot\text{O} \end{smallmatrix}\text{C}\cdot\text{NH}$, a light

yellow syrup, is prepared from isosafrole-2-imino-oxazolidine and methyl iodide (hydrochloride, m. p. 205°), the hydrolysis of which by alcoholic sodium hydroxide produces *N*-methylisosafrolealkamine (α -methylenedioxyphenylmethyl- β -hydroxypropylamine),

$\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}(\text{NHMe})\cdot\text{CHMe}\cdot\text{OH}$, m. p. 89–90° (hydrochloride, m. p. 142–144°; platinichloride, m. p. 196°; copper derivative, deep violet crystals, m. p. 151°). Dimethylisosafrole-2-imino-oxazolidine is prepared from the monomethyl compound and methyl iodide (hydriodide, thin plates, m. p. 181°), the hydrolysis of which by alcoholic sodium hydroxide produces *N*-methylisosafrolealkamine and methylamine. *N*-Acetyl-methylisosafrolealkamine, white crystals, m. p. 111–113°, and the *N*-benzoyl compound, prisms, m. p. 145–148°, are prepared from the methylalkamine. They are converted into *O*-acetyl-*N*-methyl-isosafrolealkamine hydrochloride, m. p. 182° (platinichloride, m. p. 163–169°), and the *O*-benzoyl compound, prisms, m. p. 215° (platinichloride, m. p. 170°), by passing hydrogen chloride into their ethereal solutions. *N*-Dimethylisosafrolealkamine, m. p. 71–73°, is prepared from the monomethyl compound and methyl iodide (hydrochloride, m. p. 173°; platinichloride, m. p. 190–200°); benzoyl chloride produces *O*-benzoyl-*N*-dimethylisosafrolealkamine hydrochloride, m. p. 224–226° (platinichloride, m. p. 140°). Bromoisosafrole-2-imino-oxazolidine, thin plates, m. p. 197°, is prepared by heating bromoisosafrole dibromide and carbamide at 150° (hydrochloride, m. p. 197°); on acetylation, it yields *N*-acetyl-bromoisosafrole-2-imino-oxazolidine acetate, long needles, m. p. 173–176°, which gives bromoisosafrolealkamine, prisms, m. p. 126–128°, by hydrolysis (hydrochloride, m. p. 231°; copper derivative, m. p. 158°).

III. Methylisoeugenolalkamine group. Methylisoeugenol dibromide and carbamide react to form methylisoeugenol-2-imino-oxazolidine, m. p. 153–155° (hydrochloride, m. p. 166–168°; platinichloride, m. p. 195°), which is converted into the *N*-acetyl-acetate, m. p. 155–157°, by heating with acetic anhydride; hydrolysis of the acetyl compound with 30% sodium hydroxide produces α -3:4-dimethoxyphenyl- β -hydroxypropylamine (methylisoeugenolalkamine), $(\text{OMe})_2\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{NH}_2$, thin plates, m. p. 95–96° [hydro-

chloride, m. p. 222°; platinichloride, m. p. 201°; copper compound (base), $\text{CuO} + 2\text{H}_2\text{O}$, m. p. 166–167°]. *O*-*N*-Dimethylisoeugenol-2-imino-oxazolidine, a pale yellow oil, is prepared from the imino-

oxazolidine and methyl iodide (*hydrochloride*, m. p. 144°); hydrolysis produces α -3:4-dimethoxyphenylmethyl- β -hydroxypropylamine (*dimethylisoeugenolalkamine*), hexagonal plates, m. p. 90—91° (*hydrochloride*, m. p. 190—193°; *platinichloride*, m. p. 172—174°; *copper derivative*, m. p. 138°), which gives the *hydrochloride* of the O-benzoyl derivative, m. p. 198°; the latter suffers rearrangement to the N-benzoyl derivative, m. p. 140°. α -3:4-Dimethoxyphenyl- β -hydroxypropyldimethylamine (*trimethylisoeugenolalkamine*), is a light yellow oil; the *hydrochloride* forms white nodular crystals, m. p. 149—150°.

IV. Dihydronaphthalenealkamine group. Dihydronaphthalene dibromide and carbamide react at 140° to form *dihydronaphthalene-2-imino-oxazolidine*, thin plates, m. p. 158—159° (*hydrochloride*, prismatic plates, m. p. 198°; *platinichloride*, m. p. 224°), which is converted to the N-acetyl-acetate, plates, m. p. 123—124°, and then into β -hydroxytetrahydro- β -naphthylamine (*dihydronaphthalenealkamine*), thin plates, m. p. 107—108° (*hydrochloride*, m. p. 215°; *platinichloride*, m. p. 220°; *picrate*, yellow needles, m. p. 191°; *copper derivative*, (base)₂CuO + 2H₂O, violet-red needles, m. p. 176°). *Methyldihydronaphthalene-2-imino-oxazolidine*, prepared from the above compound and methyl iodide, forms thin plates, m. p. 66—68°; *hydriodide*, m. p. 203° [*hydrochloride* (+1H₂O), m. p. 254°, anhydrous]. As by-product, an oily *isomeride* is obtained; *hydrochloride*, m. p. 235°. β -Hydroxytetrahydro- β -naphthylmethylamine, needles, m. p. 85°, is prepared from the above imino-oxazolidine derivative by hydrolysis with 20% sodium hydroxide [*hydrochloride*, m. p. 214°; *copper derivative*, (base)₂CuO, light reddish-brown crystals, m. p. 218°], which by methyl iodide is converted into β -hydroxytetrahydro- β -naphthyldimethylamine, an oil; *hydrochloride*, m. p. 224°; *picrate*, yellow plates, m. p. 160°.

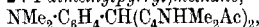
K. K.

Nitro-derivatives of Alkylated Benzidines. G. VAN ROMBURGH (*Rec. trav. chim.*, 1922, **41**, 38—43; cf. Mertens, A., 1877, 605; A., 1886, 1022; and van Romburgh, A., 1887, 245).—One of the substances obtained by the action of dilute nitric acid on dimethylaniline, at first known as *isodinitrodimethylaniline*, was shown to be a tetranitrotetramethylbenzidine, but the positions of the nitro-groups were not determined. The author considered it probable that the 3:3':5:5'-positions were occupied by these groups, and prepared the 3:3':5:5'-tetranitrotetramethylbenzidine. Tetranitro-4:4'-dimethoxydiphenyl (cf. Hirsch, A., 1889, i, 511), was treated with dimethylamine, nitrated, and boiled with phenol, the resulting product being found to be identical with the tetranitrotetramethylbenzidine first obtained. The reactions involved serve as a means for the preparation of alkylated tetranitrobenzidines. The following were prepared: 3:3':5:5'-tetranitro-diethylbenzidine, m. p. 248°, which, on treatment with concentrated nitric acid yields 3:3':5:5'-tetranitrodiphenyl-4:4'-diethyldinitroamine, long needles, m. p. 230° (decomp.); 3:3':5:5'-tetranitro-dipropylbenzidine, dark red needles, m. p. 200°, which with nitric

acid (*d* 1.49) yields 3:3':5:5'-tetranitrodiphenyl-4:4'-dipropyl-dinitroamine, small, yellow plates, exploding at 213°; 3:3':5:5'-tetranitrodiisopropylbenzidine, deep red needles, decomp. 250°, yielding with nitric acid 3:3':5:5'-tetranitrodiphenyl-4:4'-diisopropyl-dinitroamine, colourless, decomp. 209°; 3:3':5:5'-tetranitrodiisobutylbenzidine, deep red crystals, m. p. 194°, yielding with concentrated nitric acid 3:3':5:5'-tetranitrodiphenyl-4:4'-diisobutyl-dinitroamine, colourless needles, decomp. 205°; 3:3':5:5'-tetranitrodiallylbenzidine, orange-red needles, m. p. 205°, yielding on nitration 3:3':5:5'-tetranitrodiphenyl-4:4'-diallyldinitroamine, decomp. 100°. All the above nitroamines are converted into the corresponding dialkylbenzidines on treatment with boiling phenol.

H. J. E.

The Iron Salts of Dipyrrolyphenylmethane Dyes. Triphenylpyrrolylmethane. I. HANS FISCHER and VIKTORIA LUCKMANN (*Z. physiol. Chem.*, 1921, **115**, 77—93).—*p*-Dimethylaminophenyl-bis(3-acetyl-2:4-dimethylpyrrolylmethane,



is prepared by heating on the water-bath an alcoholic solution of 3-acetyl-2:4-dimethylpyrrole with *p*-dimethylaminobenzaldehyde in the presence of potassium hydrogen sulphate, and precipitated with sodium carbonate. It crystallises from ethyl acetate in tufts of slender, colourless needles, m. p. 165—166°. The ferrichloride forms brown prisms, m. p. 255° (decomp.).

Dimethylaminophenyl-bis(-3-carbethoxy-2:4-dimethylpyrrolylmethane, $\text{NMe}_2\text{C}_6\text{H}_4\text{CH}(\text{C}_4\text{NHMe}_2\text{CO}_2\text{Et})_2$, prepared from ethyl 2:4-dimethylpyrrole-3-carboxylate and *p*-dimethylaminobenzaldehyde in presence of potassium hydrogen sulphate, forms colourless, irregular leaflets, m. p. 204—205°. The ferrichloride crystallises in fine needles. *p*-Dimethylaminophenyl-bis(-3-carbethoxy-2:5-dimethylpyrrolylmethane prepared from ethyl 2:5-dimethylpyrrole-3-carboxylate and *p*-dimethylaminobenzaldehyde in presence of concentrated sulphuric acid, has m. p. 240°, and its ferrichloride has m. p. 228°. *Triphenyl-3-acetyl-2:4-dimethylpyrrolylmethane*, prepared from triphenylcarbinol and 3-acetyldimethylpyrrole by heating in glacial acetic acid, forms slender, colourless needles, m. p. 156°. *Triphenyl-3-carbethoxy-2:4-dimethylpyrrolylmethane*, obtained from triphenylcarbinol and ethyl 2:4-dimethylpyrrole-3-carboxylate crystallises in prisms, m. p. 170°. *Triphenyl-p-dimethylaminophenylmethane*, prepared from triphenylcarbinol and dimethylaniline, crystallises in slender needles, m. p. 208°.

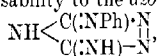
S. S. Z.

Preparation of a New Acridine Compound. LEOPOLD CASSELLA & Co., G.m.b.H. (Swiss Pat. 89241; from *Chem. Zentr.*, iv, 1010).—Formaldehyde is allowed to react with a 3:6-diamino-10-methylacridinium salt. For example, 3:6-diamino-10-methylacridinium chloride is dissolved in water and mixed with *N*-hydrochloric acid. On addition of 30% formaldehyde, a bright orange-coloured suspension is obtained. After agitation, the condens-

ation product is separated, washed with *N*-hydrochloric acid and water, and dried; it is a brick-red powder with antiseptic properties.
G. W. R.

Certain Triazoles. F. ARNDT [with E. MILDE, F. TSCHENSCHER, (FRL.) F. BRELICH, and G. ECKERT] (*Ber.*, 1922, **55**, [B], 12—18; cf. A., 1921, i, 813).—An arrangement has been reached between the author and Fromm (cf. this vol., i, 62) concerning publication in this field. The present communication is due to the fact that, in some respects, certain triazoles prepared by the authors do not harmonise in their properties with those described by Fromm in his forthcoming paper in the *Annalen*.

An alcoholic suspension of phenyldithiobiuret is converted by hydrazine hydrate and subsequent acidification with hydrochloric acid into *anilothiourazole*, $\text{NH} \begin{smallmatrix} \diagup \text{C}(\text{NPh}) \cdot \text{NH} \\ \diagdown \text{CS} \text{---} \text{NH} \end{smallmatrix}$, colourless, lustrous leaflets, m. p. 275° or somewhat higher when rapidly heated (Fromm, m. p. 268°), which is oxidised by potassium ferricyanide in alkaline solution to the *disulphide*, $(\text{NHPh} \cdot \text{C} \begin{smallmatrix} \diagup \text{N} \cdot \text{H} \\ \diagdown \text{N} \text{H} \end{smallmatrix} \text{C})_2 \text{S}_2$, yellow crystals, m. p. 233° (Fromm, m. p. 225°). *Anilothiourazole methyl ether*, $\text{NH} \begin{smallmatrix} \diagup \text{C}(\text{NPh}) \cdot \text{NH} \\ \diagdown \text{C}(\text{SMe}) \text{---} \text{N} \end{smallmatrix}$, a matt, crystalline powder, has m. p. 187—188°; the corresponding *nitrate*, m. p. 110° (decomp.), is described. *Imincanilourazole*, $\text{NH} \begin{smallmatrix} \diagup \text{C}(\text{NPh}) \cdot \text{NH} \\ \diagdown \text{C}(\text{NH}) \text{---} \text{NH} \end{smallmatrix}$, colourless leaflets, m. p. 157° (the *monohydrate* is also described), is obtained by the addition of ammonia to the acidic mother-liquors from the preparation of anilothiourazole. The constitution of the compound is deduced from its analysis, its mode of formation, amphoteric nature, convertibility into a sparingly soluble nitrate, decomp. 118°, and oxidisability to the *azo*-compound,



a pale, brownish-red powder, violent decomp., 138°. The same constitution is assigned by Fromm to a substance, m. p. 70°, prepared by the action of hydrazine on phenylthiuret; this product, however, appears to be a salt containing anilothiourazole as acidic component and two basic components, one of which, m. p. 149°, is possibly identical with aminoguanylphenylthiocarbamide, whereas the other is iminoanilourazole.
H. W.

The Significance of the Second Dissociation Constant of Uric Acid in the Equilibrium of Monourate Solutions. ARISTIDES KANITZ (*Z. physiol. Chem.*, 1921, **116**, 96—106).—A theoretical paper. Salts of uric acid formed by the action of monoacidic bases on the acid dissociate in accordance with its two stages of dissociation partly into the normal diurate salt and free uric acid as follows:

VOL. CXXII. i.

$$\frac{\text{Monourate}}{\text{Diurate} \times \text{free uric acid}} = \frac{k_1}{k_2}$$

(k_1 = constant for first stage of dissociation of the acid, k_2 = constant for second stage of dissociation of the acid). Calculated from results previously obtained by various workers k_1/k_2 = 775, or 2350. From which there is derived k_2 = 2.6×10^{-9} or 8.5×10^{-10} .

S. S. Z.

The Azo-dyes of Bilirubin. I. HANS FISCHER and HERMANN BARRENSCHEEN (*Z. physiol. Chem.*, 1921, **115**, 94—104).—A monoazo- and a diazo-product were obtained by treating bilirubin with benzenediazonium chloride. The two compounds were separated by crystallising the mixture from alcohol—the monoazo-derivative being soluble in this solvent. The monoazo-compounds, $C_{35}H_{35}O_6N_4 \cdot N:NPh$, crystallised in small, brownish-red prisms, the diazo-compound, $(C_{33}H_{34}O_6N_4(N:NPh)_2)$, in monoclinic crystals.

S. S. Z.

Colouring Matters of the Isatin-yellow Series. JH. MARTINET (*Rev. Gén. Mat. Col.*, 1921, **26**, 177—179).—When a solution of a diazonium compound is added to a solution of isatin-6-sulphonic acid in presence of sodium acetate, a hydrazone is formed, and not an azo-compound, as is shown by the stability of these compounds towards reducing agents, and by the fact that identical compounds are formed by the action of the corresponding hydrazine on isatin-6-sulphonic acid. The following hydrazones of sodium isatin-6-sulphonate in this series are described:—*Phenyldiazone*, slender, lemon-yellow needles soluble in sulphuric acid with an orange-yellow colour, isomeric with isatin-yellow (the *p*-sulphophenyldiazone of isatin). *p*-*Chlorophenyldiazone* forms yellow needles soluble in sulphuric acid with an orange-yellow colour. *o*-*Tolyldiazone* crystallises in orange-yellow needles soluble in sulphuric acid with a dark orange-yellow colour. *m*-*Tolyldiazone*, an orange-yellow, crystalline powder soluble in sulphuric acid with an orange-yellow colour. *p*-*Tolyldiazone*, rosettes of golden-yellow needles, coloured bright red by sulphuric acid and soluble with an orange-yellow colour. *m*-*Xylyldiazone* forms an orange-red powder soluble in sulphuric acid with a dark brownish-red colour. *ψ*-*Cumyldiazone*, a reddish-brown powder soluble in sulphuric acid with a dark brownish-red colour. *p*-*Ethoxyphenyldiazone*, dark yellow, felted needles soluble in sulphuric acid with a red colour. *o*-*Methoxyphenyldiazone*, dark yellow needles soluble in sulphuric acid with a red colour. *p*-*Chloro-o-methoxyphenyldiazone*, a dark yellow, crystalline powder soluble in sulphuric acid with a scarlet-red colour. *o*-*Carboxyphenyldiazone*, a lemon-yellow, crystalline powder soluble in sulphuric acid with a golden-yellow colour; the aqueous solution forms a brick-red precipitate with silver nitrate. *Diphenyl-4:4'-dihydrazone*, a brown, crystalline powder with a brownish-red reflex soluble in perchloric acid with a violet-red colour. *3:3'-Dimethoxydiphenyl-4:4'-dihydrazone*, a brown powder

soluble in perchloric acid with a violet colour. All these hydrazones are soluble in water and acetic acid, crystallise from alcohol, and their aqueous solutions are darkened slightly by alkalis. They dye wool and silk in bright yellow, orange, or red shades, and all possess a direct affinity for cotton from an alkaline bath, the affinity increasing with the molecular weight. The fastness is not great, but these colouring matters possess an interest on account of their tinctorial power, brightness, and level-dyeing properties.

In a parallel series of experiments some derivatives of isatin-5-sulphonic acid were prepared by the action of various hydrazines. *Potassium isatin-5-sulphonate phenylhydrazone*, lemon-yellow needles very soluble in water, dyes wool and silk greenish-yellow shades of low fastness. *Sodium isatin-5-sulphonate p-tolyldiazine* forms long, golden-yellow needles. *Isatin-5-sulphonic acid phenylmethyl hydrazone* forms yellow, felted needles. F. M. R.

The Free Amino-groups of the Proteins. R. ENGELAND (*Z. physiol. Chem.*, 1921, **116**, 226–227); S. EDLBACHER (*ibid.*, 228; cf. A., 1921, i, 199).—Polemical. S. S. Z.

The Optical Rotatory Power of Crystalline Ovalbumin and Serum-albumin. ELRID GORDON YOUNG (*Proc. Roy. Soc.*, 1922, [B], **93**, 15–35).—The specific rotation of crystalline ovalbumin is constant if recrystallisation is made at the isoelectric point, but varies with changes in the hydrogen-ion concentration of the solution. The constant values obtained by the author are: $[\alpha]_D^{15} - 30.81^\circ$ and $[\alpha]_E^{15} - 37.53^\circ$. The variations produced by the addition of small quantities of acid or alkali are explained on the basis of a tautomeric change of the lactam-lactim type. Crystalline horse serum-albumin was prepared by two methods. In each case the preparation had $[\alpha]_D^{15} - 62.8^\circ$ and $[\alpha]_E^{15} - 78.4^\circ$.

E. S.

The Action of Nitrous Acid on Casein. MAX S. DUNN and HOWARD B. LEWIS (*J. Biol. Chem.*, 1921, **49**, 327–341).—The distribution of nitrogen in casein and deaminised casein was determined. In agreement with the current view as to the nature of the free amino-groups in proteins, lysine was found to be absent from the hydrolysate of deaminised casein, whilst the amount of monoamino-nitrogen was correspondingly increased. Some destruction of tyrosine occurs during the deamination of casein.

E. S.

Yeast-nucleic Acid. II. H. STEUDEL and E. PEISER (*Z. physiol. Chem.*, 1921, **114**, 201–203; cf. A., 1921, i, 66).—By utilising the method of precipitating sodium guanylate with a concentrated solution of sodium acetate, it is found that a certain sample of yeast-nucleic acid contained 12–14% of this salt.

S. S. Z.

The Influence of β -Naphthalenesulphonyl Chloride on the Proteins. S. EDLBACHER and BERTHOLD FUCHS (*Z. physiol. Chem.*, 1921, **114**, 133–136).—Clupeine, salmine, sturine, thymus-

!

histone, gelatin, casein, and edestin were treated with β -naphthalene-sulphonyl chloride and the amount which combined with the respective proteins was ascertained. The basic protamines and the histone showed a relatively higher figure than the other proteins. The difference was, however, rather insignificant. The lysine content of the protein seems to have no influence on this reaction. S. S. Z.

The Titration Curve of Gelatin. DOROTHY JORDAN LLOYD and CHARLES MAYES (*Proc. Roy. Soc.*, 1922, [B], **93**, 69—85).—Determinations were made of the hydrogen-ion concentrations of solutions of gelatin in known concentrations of acid and alkali hydroxide, and the amount of combined acid or alkali hydroxide was calculated in each case. It is concluded from the results that for concentrations of acid not exceeding 0.02*N* combination occurs at the free amino-groups of the gelatin molecule; for greater concentrations of acid, however, there is probably also combination at the nitrogen of the peptide linkings. No conclusion was drawn as to the mode of attachment of alkalis. E. S.

Equilibrium: Gelatin-Hydrochloric Acid. II. ROBERT WINTGEN and HEINZ VOGEL (*Kolloid Z.*, 1922, **30**, 45—53; cf. A., 1921, ii, 247).—The hydrogen-ion concentration of mixtures of gelatin and hydrochloric acid has been determined electrometrically at 25° and the values have been compared with those calculated by means of the equilibrium formula previously published (*loc. cit.*). The acid concentration varied between 0.05*N* and 0.004*N*, and the gelatin concentration between 0° and 7%. The two sets of results agree astonishingly well, and indicate that dilute hydrochloric acid and concentrated acid combine with the same number of basic groups in gelatin, and if it is assumed that gelatin is a uniform substance, only one amino-group reacts with hydrochloric acid. It behaves therefore as a monacid base toward hydrochloric acid and has a molecular weight of 885 for the anhydrous material or 1070 for the air-dried material and an ionisation constant 5.74×10^{-11} . Turbidity and precipitation occur in the neighbourhood of the isoelectric point, and at this point solutions of 0.2% and 0.5% gelatin with *N*₃₀₀₀- and *N*₁₃₀₀-hydrochloric acid are seen in the ultramicroscope to contain numerous rapidly moving particles. The electrical conductivity of solutions of gelatin of concentrations up to 7% in 0.05*N*- and 0.025*N*-hydrochloric acid has been measured at 25° and from the results it is shown that $\Delta\kappa = 88.5$ for gelatin chloride at 25° and that the ionic conductivity of the gelatin ion is 13. Comparative measurements with β -glutin show that the power of this substance to combine with hydrochloric acid does not differ essentially from that of gelatin and that β -glutin has a molecular weight of about one-half that of gelatin. J. F. S.

Vitamins from the Point of View of Structural Chemistry. R. R. WILLIAMS (*J. Ind. Eng. Chem.*, 1921, **13**, 1107).—3-Hydroxy-

pyridine, which exists in two crystalline modifications, is shown by titration with bromine to be non-enolic in neutral solution, like the 2- and 4-compounds. It forms a 1-methyl ether which is a viscous oil miscible with water in all proportions and not volatile in steam. Its physiological action is not established. Three modifications of 4-phenylisocytosine were obtained, two of which had identical melting points and crystallographic properties, but differed greatly in their solubility in alcohol. Two freshly prepared modifications, which seemed to be Johnson and Hill's β - and δ -forms, were fed to pigeons and all the birds receiving the β -form lost weight less rapidly than those receiving the δ -form. After being kept for two months, however, the same two preparations showed no physiological difference. The author considers that vitamin-B will eventually be found to be a cyclic nitrogen compound in some ways analogous to the above. H. C. R.

Vitamins from the Point of View of Physical Chemistry. VICTOR LAMER (*J. Ind. Eng. Chem.*, 1922, **13**, 1108—1110).—The amount of vitamin-A in skim milk is roughly equal to that contained in the fat layer. The water-soluble vitamin-B is also somewhat soluble in fatty oils. Vitamin-B is absorbed by Fuller's earth and by dialysed iron, and blood charcoal removes a measurable amount of vitamin-C from orange juice; the extent of adsorption is very sensitive to changes in the hydrogen-ion concentration. Vitamin-C is partly retained on filtration through Chamberland candles. The destruction of the antiscorbutic vitamin by heat is a chemical reaction the velocity of which is accelerated by increase of temperature according to the equation $X = K\sqrt{t}$, where X is the per cent. of destruction, t the time in hours, and values of K are 0.26, 0.39, and 0.49 for 60°, 80°, and 100°, respectively. These data exclude the possibility that vitamin-C is of a protein- or enzyme-like nature. Heating at a reduced hydrogen-ion concentration results in an increased velocity of destruction. Bubbling oxygen through the solution at 100° results in the complete destruction of the vitamin in one hour, both in acid and weakly alkaline solution. Bubbling hydrogen through causes somewhat greater destruction than when no gas was used. H. C. R.

Chloroform and Pepsic Digestion. A. ASTRUC and E. RESAUD (*J. Pharm. Chim.*, 1922, [vii], **25**, 81—87).—Chloroform has only a very slow destructive influence on the diastatic activity of pepsin, whilst chloroform vapours have no appreciable action. Chloroform water is a suitable solvent for pharmaceutical preparations of pepsin, and exerts a distinct preservative action, although after two months a small decrease in the fermentative activity can be detected. Chloroform water is, however, a bad digestive medium, and considerably retards digestion *in vitro*, but it would not be correct to deduce therefrom that in the stomach it also exerts an opposing influence on digestion and the activity of the pepsin. G. F. M.

The Influence of Reaction on the Action of Trypsin. I. W. E. RINGER (*Z. physiol. Chem.*, 1921, **116**, 107—128).—The optimum H-ion concentration for the action of trypsin at 37° was under certain conditions found to be P_H 11.3. It was also found that strongly acid solutions inactivated the enzyme. At a H-ion concentration of P_H 3.15 trypsin could be kept at 37°. As the H-ion concentration diminished the inactivation became more marked. At $P_H=12$ the enzyme was almost instantaneously destroyed. The maximum imbibition of fibrin took place at a reaction which had an instantaneous inactivating action on trypsin.
S. S. Z.

The Inactivation of Trypsin. I. II. The Equilibrium between Trypsin and the Inhibiting Substance formed by its Action on Proteins. III. Spontaneous Inactivation. JOHN H. NORTHOPE (*J. Gen. Physiol.*, 1921, **4**, 227—244, 245—260, 261—274).—The decomposition of gelatin by trypsin was investigated quantitatively by conductivity determinations and also by formal titration. Inactivation of trypsin is not effected by amino-acids or by the products of the hydrolysis of proteins by acid or alkali. The inhibiting substance occurs in the products of trypsin digestion and is dialysable. The equilibrium between the inhibitor and trypsin is found to agree with the scheme, trypsin+inhibitor \rightleftharpoons trypsin-inhibitor; it is reached instantaneously and is independent of the substrate concentration. On the assumption that hydrolysis is proportional to the concentration of free trypsin, it is shown that the laws of mass action are applicable. There is no evidence for any appreciable combination of trypsin with gelatin. Spontaneous inactivation of trypsin is also shown to occur independently of the influence of hydrolytic products. The rate of this inactivation approximates closely to that demanded by a unimolecular reaction. Trypsin digestion products in excess exert a protective effect by inhibiting spontaneous inactivation.
G. W. R.

Maltase. III. The Non-identity of Maltase and α -Glucosidase. RICHARD WILLSTÄTTER and WERNER STEIBELT (*Z. physiol. Chem.*, 1921, **115**, 199—210; cf. A., 1920, i, 795; 1921, ii, 72).—A number of preparations and yeasts have given quotients for the time value for glucosidate:time value for maltase, of varying magnitudes. The two enzymes are therefore not identical.
S. S. Z.

Effect of certain Antiseptics on the Activity of Amylases. H. C. SHERMAN and MARGUERITE WAYMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 2454—2461).—Low concentrations of chloroform did not affect the activity of commercial pancreatin or malt extract, but did affect the purified preparations of these amylases. Toluene had very little influence on the activities of the amylases either in their commercial or purified condition. All the preparations studied, either commercial or purified, were injured by formaldehyde even in low concentrations, and they were all very sensitive to copper sulphate. The percentage loss of enzyme action due to

these two antiseptics did not depend on the ratio of antiseptic to enzyme or to substrate, but on the concentration of the antiseptic in the system. The sensitiveness of the amylases to formaldehyde or copper sulphate as compared with their sensitiveness to toluene is possibly connected with the protein nature of the enzymes.

W. G.

The Influence of certain Amino-acids on the Enzymic Hydrolyses of Starch. H. C. SHERMAN and FLORENCE WALKER (*J. Amer. Chem. Soc.*, 1921, **43**, 2461—2469).—Previous work (cf. this vol., i, 66) has been extended to a study of glycine, alanine, tyrosine, and phenylalanine, using, however, Lintner's soluble starch as the substrate. Addition of any of these amino-acids caused an increase in the rate of hydrolysis of starch by purified pancreatic amylase, commercial pancreatin, saliva, or purified malt amylase, but less marked results were obtained with malt extract, taka-diastase, or an *aspergillus* amylase. The addition of two of these amino-acids produced no greater effect than would result from the same concentration of one of them. The favourable effect of the added amino-acid was not due to any alteration in hydrogen-ion concentration of the medium or to the combination of the amino-acid with the product of the enzyme action. It is probably due, in part at least, to a protection of the enzyme from deterioration in the aqueous dispersion in which it acts. The addition of these amino-acids is a very effective means of protecting the enzyme from the deleterious action of copper sulphate (cf. preceding abstract) and may even serve to restore to full activity an enzyme which has been partly inactivated by copper sulphate.

W. G.

The Influence of Arginine, Histidine, Tryptophan, and Tyrosine on the Hydrolysis of Starch by Purified Pancreatic Amylase. H. C. SHERMAN and MARY L. CALDWELL (*J. Amer. Chem. Soc.*, 1921, **43**, 2469—2476).—The amylolytic power of purified pancreatic amylase on soluble starch was measured in the presence of these amino-acids, using glycine and phenylalanine as control amino-acids (cf. preceding abstract). Arginine and cystine markedly influence the digestion of starch, but histidine and tryptophan do not. It is again shown (*loc. cit.*) that the results obtained were not due to any variation in the hydrogen-ion concentration of the medium. There are thus apparently specific effects due to the amino-acids studied, which may depend on the nature of these acids and thus discriminate their action from that of the monoamino-acids originally studied.

W. G.

Remarks on the Elution of Saccharase and Maltase from Adsorbed Substances. RICHARD WILSTÄTTER and RICHARD HENNING (*Z. physiol. Chem.*, 1921, **116**, 53—66).—Monosodium phosphate accelerates the elution of adsorbed saccharase from silica with a solution of sucrose. A phosphate mixture of similar composition has the same effect. This is not due either to the definite concentration or to the specific action of the phosphate,

as a citrate buffer of $P_H=4.5$ produces a similar acceleration but not an acetate buffer of this H-ion concentration. Primary phosphate has also an influence on the elution. Very low concentrations of glycerol sometimes raise the extracting power of primary phosphates. Maltase solutions do not remove adsorbed saccharase from alumina, but they can do so in the presence of monosodium phosphate. Maltase is not extracted by maltose alone, but is extracted by maltose in the presence of a buffer mixture. S. S. Z.

The Specific Nature of Saccharase and Raffinase. RICHARD WILLSTÄTTER and RICHARD KUHN (*Z. physiol. Chem.*, 1921, **115**, 180—198).—The quotient for time value for raffinase/time value for saccharase for several preparations of inverting enzymes was found to be 11.3. Similar quotients were also worked out for a number of yeasts. It is therefore concluded that saccharase and raffinase are two different enzymes. From the constant quotient obtained with the various inverting preparations it may be assumed that the two enzymes show a great similarity in some of their physical properties and are therefore not amenable to fractionation. S. S. Z.

The Regeneration of Inactivated Saccharase by Dialysis. HANS V. EULER and OLOF SVANBERG (*Z. physiol. Chem.*, 1921, **114**, 137—148).—Saccharase inactivated by silver nitrate, mercuric chloride, or aniline can be regenerated by dialysis. Whilst in the case of the metal salts the total regeneration of the enzyme cannot be accomplished, saccharase inactivated by the action of aniline can have its entire activity restored by dialysis. The saccharase of an active dry preparation could not be extracted with aniline. S. S. Z.

Rennet Coagulation of Milk as a Stimulated Process. EMIL BAUR and EUGEN HERZFELD (*Z. physikal. Chem.*, 1921, **98**, 460—473).—The velocity of coagulation of milk by rennet of various concentrations has been determined at 37° with the object of ascertaining whether the process is stimulated, and whether the rennet concentration is augmented by rennet contained in the milk. The results show that the coagulation is accompanied by an autocatalytic formation of new rennet in the milk. Experiments have been made to ascertain the rate at which the reaction is transmitted through milk in which no rennet has been placed. The reactions were carried out in a capillary tube which was connected with a large tube containing milk and rennet. The rate of transmission of the reaction is found to be 0.8 cm./hour. A control experiment shows that diffusion would have occasioned only a transmission of 1.0 ± 0.5 cm. in hours. J. F. S.

Oxydases. A. W. VAN DER HAAR (*Chem. Weekblad*, 1922, **19**, 33—34).—The failure of Wester (*ibid.*, 1921, **18**, 700—703) to detect a blue coloration with guaiacol in alcohol may be due to the presence of reducing saccharides; after removal of these by dialysis, the blue colour is readily obtained. Priority is claimed for the

author (A., 1910, i, 604; 1917, i, 301) for observations as to the chemical nature of the oxydase molecule advanced by Willstätter and Stoll.. S. I. L.

Tannase. KARL FREUDENBERG and ERICH VOLLBRECHT (*Z. physiol. Chem.*, 1921, **116**, 277—292).—For the preparation of tannase the mould (*Aspergillus niger*!) was grown on a medium consisting of myrobalan extract, dipotassium phosphate, ammonium sulphate, and magnesium sulphate. After about four days' growth it was extracted with water, care being taken that the acid was neutralised with barium hydroxide during the extraction. The extract was then concentrated in a vacuum and the enzyme precipitated with absolute alcohol. The conditions under which tannase can be estimated quantitatively, using methyl gallate as the substrate, were also worked out. S. S. Z.

Reactions of the Phosphazines. WALTER THEODORE KARL BRAUNHOLTZ (T., 1922, **121**, 300—305).

Action of Arsenious Chloride on Aniline. JOHN H. SCHMIDT (*J. Amer. Chem. Soc.*, 1921, **43**, 2449—2454).—Aniline reacts with arsenious chloride in solution in *n*-heptane to give a yellow compound, *trianilinearsine hydrochloride*, $\text{As}(\text{NHPh}, \text{HCl})_3$, m. p. 148—150°, which is probably identical with the compound described by Schiff (*Compt. rend.*, 1863, **56**, 268, 1095). This compound is readily transformed by heating it, either alone or preferably with an excess of aniline, into cyclic arsenic compounds. The first product is chlorophenarsazine, which with alkalis gives *phenarsazine oxide*, $\text{O}(\text{As} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{NH})_2$, and this on oxidation with hydrogen peroxide in alkaline solution yields *phenarsazinic acid*, $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{AsO} \cdot \text{OH}$. From this acid, on nitration, *dinitrophenarsazinic acid* was obtained, giving a *disodium* salt. *Aniline arsenate*, m. p. 147—148°, and *dianiline arsenate*, m. p. 143°, were obtained by the interaction of aniline and syrupy arsenic acid in alcoholic solution, using excess of aniline or acid according to the salt required.

A simple arrangement for sublimation in a vacuum, using a Beckmann boiling apparatus, is described. W. G.

Organo-derivatives of Thallium. IV. Action of Thallium Chlorides on the Grignard Reagent and on Organo-derivatives of Tin, Lead, and Bismuth. DOROTHY GODDARD and ARCHIBALD EDWIN GODDARD (T., 1922, **121**, 256—261).

Physiological Chemistry.

Physiology of the Respiration of Fishes in Relation to the Hydrogen-ion Concentration of the Medium. EDWIN B. POWERS (*J. Gen. Physiol.*, 1921, 4, 305—317).—The absorption by marine fishes of oxygen at low tension is dependent on the hydrogen-ion concentration of sea-water. It is suggested that variations in the ability of individuals of a species to absorb oxygen at a given hydrogen-ion concentration depend on the alkaline reserve of the blood.
G. W. R.

The Respiratory Processes in *Mya arenaria* and other Marine Mollusca. J. B. COLLIP (*J. Biol. Chem.*, 1921, 49, 297—310).—From experiments on the survival of *Mya arenaria* under anaerobic conditions, it is concluded that this, and other calcareous shelled molluscs, have in their tissues a store of oxygen which suffices temporarily to replace the external supply of the latter. Under anaerobic conditions the normal acid-base balance is maintained by the mobilisation of the reserves of calcium in the liver and the shell.
C. R. H.

The Action of Intravenous Injections of Hypertonic Solutions of Various Sugars on the Respiratory Metabolism of the Dog. MAX BÜRGER (*Biochem. Z.*, 1921, 124, 1—24).—Within half an hour of the intravenous injection of hypertonic solutions of dextrose and levulose, the respiratory quotient rises to a value above 0.9 with simultaneous increased heat production. The relatively greater heat production after levulose points to direct utilisation of the sugar without previous conversion into glycogen. The considerably smaller effects of intravenous injection of hypertonic lactose and sucrose solutions is an indirect effect, and is attributed to an increased kidney and heart activity produced by flow of tissue fluids into the blood owing to the action of the hypertonic carbohydrate solutions.
H. K.

The Influence of Lack of Calcium in the Diet on the Respiratory Basal Metabolism. FAUSTO PEDOTTI (*Biochem. Z.*, 1921, 123, 272—283).—Rats fed on a diet deficient in calcium show a diminished respiratory basal metabolism.
H. K.

The Physiology of the Glands. XLVIII. Experiments on the Respiratory Metabolism of the Dog with Extirpated Spleen. LEON ASHER and CHU KODA (*Biochem. Z.*, 1921, 122, 154—160).—The gaseous metabolism on a normal diet of dogs which have had their spleens removed is normal. This differs from the results of others on rats and rabbits.
H. K.

The Physiology of the Glands. XLIX. The Respiratory Interchange of the Dog with Extirpated Spleen and Diet Deficient in Iron. LEON ASHER and FRANCIS H. DOUBLER (*Biochem. Z.*, 1921, 122, 161—167).—Extirpation of the spleen

coupled with an iron-free diet has no action on the respiratory gaseous metabolism or the coagulation time of the blood of the dog. The hæmoglobin content of the blood falls off very slowly.

H. K.

The Action of Carbon Dioxide on Salt and Water Distribution in Blood. G. MUKAI (*J. Physiol.*, 1921, **55**, 356—370; from *Physiol. Abstr.*, 1922, **6**, 568).—On treatment with carbon dioxide, the chlorine and water content of the corpuscles increases, the former by anion interchange, the latter by osmosis consequent on the increased carbon dioxide and chlorine in the corpuscles. Corpuscles always contain more carbon dioxide than the corresponding serum; the carbon dioxide is carried partly by increased alkali and partly by proteins. There is presumptive evidence that the corpuscles were alive for more than six hours in these experiments.

E. S.

The Distribution of Chlorine in the Blood. S. VAN CREVELD (*Biochem. Z.*, 1921, **123**, 304—314).—The results of recent workers on the distribution of chloride in the blood are criticised. Direct estimation on the circulating blood shows that the corpuscles are permeable; the percentage of chloride in the corpuscles relative to that of the plasma is greater in venous than in arterial blood. There is no evidence of a fixation of chloride as a fibrinogen chloride compound.

H. K.

Relation between the Chloride Content of the Blood and its Volume per cent. of Cells. A. NORGÅRD and H. C. GRAM (*J. Biol. Chem.*, 1921, **49**, 263—278).—Estimations were made of the chloride content of whole blood and plasma in normal and pathological cases. Nearly constant values were obtained for the plasma in all cases, whilst the values for whole blood were found to be dependent on the cell volume percentage, the smaller the latter the greater being the chloride content of the blood. Calculations of the chloride content of the corpuscles yielded, with one exception, constant values.

E. S.

The Fate of Sulphides in the Blood. HOWARD W. HAGGARD and THOMAS J. CHARLTON (*J. Biol. Chem.*, 1921, **49**, 519—529).—The toxic properties of hydrogen sulphide are due neither to the formation of a compound with the hæmoglobin of the blood nor to the production of sodium sulphide in the plasma. On the contrary, in vitro and in vivo experiments show that sodium sulphide is rapidly and completely hydrolysed by blood, the resulting hydrogen sulphide being quickly oxidised in the presence of oxygen. The toxic effects of hydrogen sulphide, and consequently of sodium sulphide, are not cumulative.

E. S.

The Isolation of Amino-acids in Blood. EMIL ABDERHALDEN (*Z. physiol. Chem.*, 1921, **114**, 250—254).—The presence of all the known amino-acids was established in the serum and in the plasma of cattle and horses by examining the dialysates of these fluids. Substances, on the other hand, giving the biuret reaction

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or substances consisting of more than one amino-acid could not be found in the dialysate of these plasmas and serums. S. S. Z.

Blood Acetone Substances after the Injection of Small Amounts of Adrenaline Chloride. ROGER S. HUBBARD and FLOYD R. WRIGHT (*J. Biol. Chem.*, 1921, 49, 385—388).—After injection of adrenaline there is a rise in the concentration of acetone substances in the blood, which, however, bears no apparent relation to changes in the blood-sugar concentration or carbon dioxide-combining power. C. R. H.

Fibrinogen Content of Human Blood. H. C. GRAM (Pamphlet, Copenhagen, 1921, pp. 276; from *Physiol. Abstr.*, 1922, 6, 566; cf. this vol., ii, 240).—A method of estimating fibrinogen in 2 c.c. of citrated blood after adding calcium chloride is described. In normal adults the plasma yields 0.2 to 0.38%; in whole blood the figures are 0.11 to 0.19. A number of diseases are mentioned in which variations occur. E. S.

Animal Calorimetry. XIX. The Influence of Acids on the Carbon Dioxide-combining Power of the Blood Plasma. SOPHIA A. TAISTRA (*J. Biol. Chem.*, 1921, 49, 479—483).—Measurements of the carbon dioxide-combining power of the blood indicate that the specific dynamic action of foodstuffs is not dependent on neutralisation of the alkaline reserve of the blood. E. S.

Animal Calorimetry. XX. The Influence of the Ingestion of Meat and of Glycine and Alanine on the Carbon Dioxide-combining Power of Blood Plasma. ALFRED CHANTUTY (*J. Biol. Chem.*, 1921, 49, 485—486).—The ingestion of meat, glycine, or alanine in a dog increases the alkali reserve of the blood plasma as measured by its carbon dioxide-combining power. E. S.

The Flocculating Capacity of Human Blood-plasma. WILHELM STARLINGER (*Biochem. Z.*, 1921, 123, 215—224).—Flocculation in blood-plasma, produced, for example, by saturated sodium chloride solution, can be used as a measure of fibrinogen content. Inhibition of flocculation is produced by acid, alkali, neutral salts, increase of temperature, pepsin, and Witte peptone, whilst agar, gum-arabic, gelatin, and glycine increase flocculation. H. K.

The Influence of Potassium and of Radioactivity on the Oxidation Velocity of the Red Corpuscles. PHILIPP ELLINGER (*Z. physiol. Chem.*, 1921, 116, 266—276).—The presence of potassium in the surrounding medium is indispensable for the respiratory function of the red blood-corpuscles. It can be replaced by rubidium, but not by caesium. Radioactive substances emitting α -rays cannot replace potassium in the respiratory function of the corpuscles. Eosin has a stimulating action in low and an injurious action in high concentrations. Fluorescein has an injurious action even in very low concentrations. The stimulating influence of eosin is independent of the action of potassium. S. S. Z.

Permeability of the Red Blood-corpuscles. E. WIECHMANN (*Deuts. med. Woch.*, 1921, 47, 824—825; from *Physiol. Abstr.*, 1922, 6, 565; cf. this vol., i, 80).—The rapidity with which the exchange of ions occurs depends on specific properties of the ions themselves.
E. S.

The Analysis of a Volume Curve of Blood-corpuscles in Hypertonic Solutions, which renders possible the Simultaneous Differentiation of Osmotic and Colloido-chemical Changes in Volume. TAKEO TAKEI (*Biochem. Z.*, 1921, 123, 104—127).—Blood-corpuscles of men, rabbits, and oxen shrink in hypertonic solution proportionally to the external osmotic pressure, when this pressure does not exceed four times the normal pressure, quite independently of the nature of the medium. Beyond this point there is a sudden increase of corpuscular volume which may almost reach the initial normal volume. This is ascribed to a swelling of the erythrocyte colloids. The shrinkage is a reversible process, but the swelling is irreversible, as haemolysis takes place on dilution. In serum rendered hypertonic by dextrose there is no swelling of the corpuscles.
H. K.

The Biochemistry of the Phosphatides and Sterols. IV. The Importance of the Proportion of Cholesterol-Lecithin of the Erythrocyte Surface for the Stability of Suspensions of Blood-corpuscles and for Natural Haemolysis. R. BRINKMAN and (FRL.) H. WASTL (*Biochem. Z.*, 1921, 124, 25—36).—In salt solutions, corpuscles lose their distinctive velocity of sedimentation owing to a washing away of constituents of the surface of the corpuscles. These constituents may be recovered as a cholesterol (light petroleum soluble) fraction and a phosphatide (alcohol-soluble) fraction. If both be added to the washed corpuscles, they recover their property of agglutination, whereas if only phosphatides be added there is haemolysis.
H. K.

Agglutination and Velocity of Sedimentation of Corpuscles. II. WILHELM STARLINGER (*Biochem. Z.*, 1921, 122, 105—119).—The addition of kaolin, bohus alba, or animal charcoal retards the sedimentation of corpuscles by adsorbing the fibrinogen. Gelatin, agar, and gum, however, accelerate the flocculation and sedimentation. This is attributed to a diminution of the suspension stability of the corpuscles, due partly to abstraction by adsorption by these substances of the break-down products of the corpuscles and partly to withdrawal of water.
H. K.

The Action of some Electrolytes and Non-Electrolytes on the Velocity of Sedimentation of the Red Blood-corpuscles of the Horse. J. RENNSTRÖM (*Biochem. Z.*, 1921, 123, 1—26).—The velocity of sedimentation of horse corpuscles was determined in presence of various salts, hydrochloric acid, serum, gelatin, and narcotics. The results obtained show great variation, and are interpreted on the hypothesis that the action of ions is due to adsorption on the surface of the corpuscle, the presence of colloids

modifying the adsorption of the ions through competition for the erythrocyte surface. H. K.

The Distribution of Chloride between Corpuscles and Plasma. AUGUSTIN MURESANU (*Biochem. Z.*, 1921, 124, 114—118).—In agreement with other observers, the corpuscles were found to be practically free from chloride. The contrary statements of Siebeck (*Arch. expt. Path. Pharm.*, 1920, 85, 214), even employing Siebeck's method, could not be substantiated. In some pathological cases, for instance, nephritis, the corpuscles contain appreciable quantities of chloride. H. K.

Permeability of Cells and Tissues. VIII. The Question of the Distribution of Hormones and Drugs in the Blood. HANS SCHAEFFI (*Biochem. Z.*, 1921, 122, 232—250).—The distribution of barium chloride, choline bromide, and nicotine between corpuscles and plasma or serum was determined by a physiological method—using Fuhner's nerve-free leech preparation. The corpuscles are impermeable to barium, but nicotine and choline both distribute themselves equally in plasma or serum and corpuscles. H. K.

The Fixation of Quinine by Red Blood-corpuscles and the Distribution of Quinine in Blood. P. RONA and E. BLOCH (*Biochem. Z.*, 1921, 121, 235—258).—By making use of the relation, that when the toxic concentration of quinine on the activity of serum lipase is increased in geometrical progression the velocity constants of the hydrolysis of tributyrin by lipase fall off in arithmetical progression, the authors find that 80 to 90% of the quinine added to blood is fixed by the corpuscles. The method is applicable to fractions of a mg. of quinine. After intravenous injection of quinine, only 1 to 4% of the quinine could be found in the blood. H. K.

The Distribution of Cinchona Alkaloids in the Organism. II. ALFRED SCHNABEL (*Biochem. Z.*, 1921, 122, 285—294).—Further experiments with kidney and brain suspensions and optochin show the same behaviour as earlier experiments with corpuscles. The optochin is taken up by the cells and slowly given up to the surrounding fluid. Parallel with this behaviour in vitro, it is found that freshly defibrinated blood of a rabbit injected with optochin has a lower concentration of optochin in the serum when examined immediately than when kept for some time. The fixation of optochin by corpuscles is an adsorption phenomenon. Quinine, which can also be estimated by its inhibitory action on the reducing capacity of pneumococci to methylene-blue, but is about one-twentieth as active as optochin, is likewise taken up by the corpuscles and slowly given off to the surrounding fluid, producing an actual increased concentration of quinine in the surrounding fluid. H. K.

The Theory of Blood-clotting. ALBERT FUNCK (*Biochem. Z.*, 1921, 124, 148—155).—Flocculation of fresh undialysed

fibrinogen only takes place between P_H 4 and P_H 9. At an acidity greater than P_H 4, fibrinogen wanders to the cathode and at an alkalinity greater than P_H 9 to the anode. Purified solutions of serum-albumin, serum-globulin, and egg-albumin cause clotting of fibrinogen but fibrino-globulin is without action. H. K.

The Quantitative Action of some Factors in the Clotting of Blood. LUDWIG HELLER (*Biochem. Z.*, 1921, **123**, 90—103).—At a lower concentration than about 10%, normal blood does not clot. At a blood-dilution of 1:200, the minimum concentration of calcium chloride necessary for clotting is 0.005 to 0.006%; at higher dilutions, the minimal calcium chloride concentration is higher, and at lower dilutions of the blood, lower. The concentration of sodium chloride is also of influence. The results are applied to the blood of pathological cases. H. K.

The Free and Esterified Sulphuric Acid in Normal and in Pathological Body-fluids. WOLFGANG HEUBNER and ROBERT MEYER-BISCH (*Biochem. Z.*, 1921, **122**, 120—127).—Normal serum contains about 0.02% of sulphate which can be dialysed out with the chlorides, but is adsorbed by the proteins when these are precipitated. In pathological exudates there was one-third less sulphation than in serum and a small proportion of sulphuric acid in ester form. The latter shows an increase after sulphur injections in diseases of the joints. H. K.

Fixation of Lime by Animal Tissues. VI. E. FREUDENBERG and P. GYÖRGY (*Biochem. Z.*, 1921, **124**, 299—310).—A number of bases and basic substances inhibit the fixation of calcium by cartilage or serum. The action of anions on the fixation of calcium by serum and brain-matter has also been examined. H. K.

Physico-chemical Investigations on Body-fluids. IV. The State of Sugar in Serum. STEFAN RUSZNYÁK and GÉZA HERÉNYI (*Biochem. Z.*, 1921, **121**, 125—126).—The reducing substances present in serum are greater in amount than in the ultrafiltrate. After fermentation with yeast, the residual reducing substances in the serum are equal in amount to those in the ultrafiltrate. A portion of the original sugar of the serum is therefore in a colloidal, non-ultra-filtrable state. H. K.

"Double-nitrogen," a Diagnostic for Endogenous Protein-breakdown, especially for Hidden Suppuration. ARNOLD HAHN (*Biochem. Z.*, 1921, **121**, 262—272).—The difference between the nitrogen content of serum after removal of proteins and breakdown products by precipitation with phosphotungstic acid and the nitrogen content of serum after removal of proteins alone by trichloroacetic acid, gives a measure of the protein degradation products present. This value the author terms "double-nitrogen" (Doppelstickstoff). H. K.

The Action of Kaolin on the Terminal Component and on the Tributyrin Hydrolytic Capacity of Guinea Pig's Serum. O. OLSEN (*Biochem. Z.*, 1921, **124**, 119—129).—Previous experiments (*ibid.*, **112**, 188) showed an analogy between the final portion of the complement and the tributyrinase, rather than with the middle portion, or the third component of the complement. By gentle agitation of sera with kaolin, it is now shown that the final portion of the complement is inactivated before the tributyrinase. It is thought that the final portion of the complement may be complex, the tributyrinase constituting one component. H. K.

Hæmolytic Action of Sodium Glycocholate. ERIC PONDER (*Proc. Roy. Soc.*, 1922, [B], **93**, 86—103).—Serum-albumin, peptone, adrenaline, pituitrin, histamine, and histidine accelerate or retard the hæmolytic activity of sodium glycocholate according as they are added after or before the latter to the suspension of blood cells. The author is unable to explain these results on the theory that the bile salt dissolves the corpuscle envelope, but suggests that they are due to a disturbance of surface tension at the surface of the corpuscle. Blood-serum inhibits the hæmolytic action of both sodium taurocholate and sodium glycocholate. E. S.

Animal Calorimetry. XVIII. The Behaviour of Various Intermediary Metabolites on the Heat Production. GRAHAM LUSK [with JAMES EVENDEN] (*J. Biol. Chem.*, 1921, **49**, 453—478; cf. A., 1919, i, 105).—No change in metabolism was produced by the administration of sodium hydrogen carbonate to a dog. Increased heat production was, however, observed in each case after administration of the following substances: acetic acid, lactic acid, sodium lactate, glycollic acid, sodium glycolate, hydrochloric acid, sodium salt of glycine. There was no relation between the potential hydrogen-ion concentration and the specific dynamic action of the substances administered. E. S.

The Hydrolysis of Casein and Deaminised Casein by Proteolytic Enzymes. MAX S. DUNN and HOWARD B. LEWIS (*J. Biol. Chem.*, 1921, **49**, 343—350).—Deaminised casein is hydrolysed by pepsin and trypsin, but is unattacked by erepsin except after the preliminary action of either of the first-named enzymes. In each case, the action proceeds at a slower rate than in the corresponding case of casein. Experiments on a dog indicate that it is metabolised in the animal body, although repeated ingestion produces vomiting and loss of appetite. E. S.

The Problem of Nuclein Metabolism. II. The Influence of Human Fæces on Yeast-nucleic Acid. JULIUS ROTHER (*Z. physiol. Chem.*, 1921, **114**, 149—160; cf. A., 1920, i, 784).—Approximately one-half of the purine bases of yeast-nucleic acid have their purine rings ruptured when the acid is digested for forty to forty-eight hours at 37° with a suspension of human fæces. In a metabolic experiment with a human being, it was found that the purine ring of the bases given to the patient per os in the form

of yeast-nucleic acid was ruptured in the lower portion of the intestine. The reaction depends on the time of sojourn of the nucleic acid in the large intestine. S. S. Z.

Synthesis of Uric Acid in the Human Organism. GUSTAV KOLLMANN (*Biochem. Z.*, 1921, **123**, 235—244).—Observations on a twenty-six year old girl for fifty days on a standard diet poor in purines resulted in an increase of weight of 4 kilograms and an excretion of 15 grams of uric acid in excess of the quantity furnished by the food. A purine synthesis is postulated, but requires further confirmation. H. K.

The Formation of Mercapturic Acid during the Ingestion of a Protein Minimum. JOSEPH KAPFHAMMER (*Z. physiol. Chem.*, 1921, **116**, 302—307).—During the ingestion of a protein minimum, added bromobenzene is converted into *p*-bromophenyl-mercaptopuric acid if at the same time cystine is introduced subcutaneously. S. S. Z.

The Action of the Thyroid Gland Hormone in Phloridzin Diabetes. XLVI. LEON ASHER and WALTER HERRISBERGER (*Biochem. Z.*, 1921, **121**, 64—75).—Phloridzinised rats show an increased basal metabolism on administration of desiccated thyroid. H. K.

Vitamin-B and Co-enzymes. II. H. V. EULER and KARL MYRBACK (*Z. physiol. Chem.*, 1921, **115**, 155—169).—A method is described by means of which vitamin-B ("Biocatalyst") is estimated quantitatively by its stimulating power on alcoholic fermentation. A maximum is reached by the addition of the stimulating substance after which any further addition inhibits the fermentation. Utilising this method, it is found that a considerable quantity of the vitamin is used up in the human body per day. S. S. Z.

Increase of Nitrogen after Fleshy and Meal Diets. L. DIENES (*Biochem. Z.*, 1921, **123**, 128—143).—After emaciation, more nitrogen is fixed from fleshy foods than from wheaten flour. H. K.

Replacement of Protein by Urea in Rations. A. MORGEN, G. SCHÖLER, K. WINDHEUSER, and ELSA OHLMER (*Landw. Versuchs.-Stat.*, 1921, **99**, 1—26).—Experiments with sheep and milch animals showed that in rations containing a normal amount of protein, replacement by urea is possible up to 30—40%. A slight depression in milk production in the case of milch sheep and goats receiving a portion of their nitrogen in the form of urea was balanced by an improvement in the quality of the milk. G. W. R.

Colorimetric Experiments on Tryptophan. VI. The Tryptophan Content of some Foods and the Tryptophan Requirement of Men. OTTO FÜRTH and FRITZ LIEBEN (*Biochem. Z.*, 1921, **122**, 58—85; cf. A., 1921, i, 64; 74; ii, 71).—For the purpose of this investigation, the tryptophan content of a large

number of foodstuffs had to be determined colorimetrically (Voisenet's test). As the presence of a large proportion of fats or starch interferes with the reaction, the proteins had to be isolated in some cases. On an average, the tryptophan content of nutritive protein is between 2% and 2.4%. By making use of the large numbers of metabolic experiments described in the literature, the authors show that a man weighing 70 kilos. consumes 2.5 to 3.2 grams of tryptophan per diem, and no harm ensues if the tryptophan content is only one-half of this. H. K.

Histochemistry of Spermatozoa. IV. Chemical Composition of the Spermatozoa of the Shad (*Clupea atosa*). H. STREUDEL (*Z. physiol. Chem.*, 1921, **114**, 161—166; cf. A., 1911, ii, 626, 905; 1913, i, 216).—The nucleic acid of the spermatozoa of the shad was prepared by the sodium acetate and alcohol method as the copper salt, $C_{43}H_{57}O_{24}N_{15}P_4Cu_2$. The amount of the salt obtained was equal to 41.47% of the total matter. The phosphorus-nitrogen ratio of the spermatozoa of the shad was found to be identical with that of the spermatozoa of the herring. S. S. Z.

Sugar Content of the Hen's Egg. J. S. HEPBURN and E. Q. ST. JOHN (*J. Amer. Inst. Homeopathy*, 1921, **14**, 339—343).—A modification of the method of Folin and Wu (A., 1919, ii, 308; 1920, ii, 337) yielded the following results for the minimum, maximum, and average percentage content of dextrose respectively: whole egg, 0.36—0.49, 0.45%; white free from yolk, 0.29—0.57, 0.47%; yolk free from white, 0.11—0.15, 0.14%; yolk commercially separated, 0.16—0.35, 0.25%. Results obtained from eggs after preservation in sodium silicate solution, and from frozen white of egg, were within the above limits, but putrid white of egg contained no dextrose. CHEMICAL ABSTRACTS.

Lipoids. XVIII. The Preparation of Phosphosulphatides from Brain. SIGMUND FRÄNKEL and OSKAR GILBERT (*Biochem. Z.*, 1921, **124**, 206—215).—The portion of protagon from human brains which forms a barium salt insoluble in alcohol is known to be free from galactosides. It contains, however, sulphur and phosphorus. A portion of the barium salts soluble in benzene was prepared and the fraction of this soluble in light petroleum is a phosphosulphatide, the ratio P:S:N:Ba being 1:1:3:2. On hydrolysis, the barium salt gave aminoethyl alcohol and cerebronic acid. H. K.

Lipoids. XIX. A Lecithin from Human Brain. SIGMUND FRÄNKEL and ARTUR KÄSZ (*Biochem. Z.*, 1921, **124**, 216—227).—Linnert's sahidin from human brain has been re-examined. At one stage of the purification the phosphorus nitrogen ratio was 3:2, in agreement with Linnert's values, but further purification by solution in toluene and precipitation with alcohol gave finally a sparingly soluble product which proved to be pure lecithin (N:P=1:1). The hydrolytic products were glycerylphosphoric acids, choline, stearic, and oleic acids. H. K.

Sugar of Cerebrospinal Fluid. R. COOPE (*Quart. J. Med.*, 1921, 15, 1—8; from *Physiol. Abstr.*, 1922, 6, 564).—A low sugar content is found in tubercular meningitis, and certainly not a high one in encephalitis lethargica, which some French writers claim.

E. S.

The Relation between Blood-plasma and Tissue Fluids, especially the Aqueous Humour and the Cerebrospinal Fluid. I. The Sugar Content and the Question of the Combined Sugar. J. DE HAAN and S. VAN CREVELD (*Biochem. Z.*, 1921, 123, 190—214).—The dextrose content of the aqueous humour and of the cerebrospinal fluid of the rabbit is less than that of the blood-plasma. In hyperglycemia produced by adrenaline, the diffusion of dextrose into the two fluids is moderately rapid and of the same order in both. The excess of dextrose in normal blood-plasma over that in the aqueous humour is attributed to the non-dialysable bound sugar, whilst the difference in the cerebrospinal fluid is augmented by the greater consumption of dextrose by the brain.

H. K.

Comparative Study of the Sugar Content of the Spinal Fluid in Diseases of the Nervous System. L. D. STEVENSON (*Arch. Neurol. Psychiatry*, 1921, 6, 292—294).—Benedict's method led to distinctly higher results than those given by Shaffer's method. Four cases of encephalitis gave an average of 60 mg. of sugar per 100 c.c. by Shaffer's method. Former values with Folin's method were much higher. It is suggested that some other reducing substance may be present in cases of encephalitis, which may not interfere with the Shaffer method.

CHEMICAL ABSTRACTS.

Chemical and Biochemical Investigations of the Nervous System under Normal and Pathological Conditions. IX. GIACOMO PIGHINI (*Biochem. Z.*, 1921, 122, 144—151).—A review of the previous results of the author and of others.

H. K.

The Thermolability of the Sucrose-splitting Enzyme of the Human Jejunum. H. VON EULER and KARL MYRBÄCK (*Z. physiol. Chem.*, 1921, 115, 68—76).—The sucrose-splitting enzyme of the human jejunum is much more thermolabile than the corresponding yeast enzyme. The two enzymes are therefore not identical.

S. S. Z.

A Basic Protein Derivative. K. FELIX (*Z. physiol. Chem.*, 1921, 116, 150—165).—Basic protein derivatives were obtained from the mucous membrane of the intestine, from the lymphatic glands, and from the thymus. They were prepared by extracting the tissues with dilute hydrochloric acid, precipitating the histone by saturating the solution with sodium chloride, and finally precipitating the basic derivative with phosphotungstic acid. The distribution of nitrogen in these derivatives has been worked out. Trypsin did not digest these substances.

S. S. Z.

The Saccharase of the Intestine. H. VON EULER and O. SVANBERG (*Z. physiol. Chem.*, 1921, **115**, 43—67).—Quantitative determinations of the enzymic activity of the intestinal saccharase in various sections of the intestine are given. S. S. Z.

Action of Potassium, Calcium, and Magnesium Ions on the Sympathetic Nerve of the Heart. J. TEN CATE (*Arch. Néerland. physiol.*, 1921, **6**, 269—288).—Frogs' hearts perfused with Ringer solution containing magnesium, or excess of potassium or calcium, or from which potassium is omitted, respond to excitation of the accelerator nerve or to the action of adrenaline after they have ceased to beat. The same holds if the Ringer solution is replaced by an isotonic solution of common salt, but there is no response when calcium-free Ringer is used. The possible explanation is discussed. E. S.

Potassium and Radioactivity. S. G. ZONDEK (*Biochem. Z.*, 1921, **121**, 76—86).—Using a Straub's heart preparation, the author failed to confirm any of Zwaardemaker's observations (*A.*, 1918, i, 326). Zwaardemaker's success is attributed to the use of antiquated methods. H. K.

The Ionic Equilibrium of Cells. The Physiology of Sodium. S. G. ZONDEK (*Biochem. Z.*, 1921, **121**, 87—108).—Hearts were perfused with various concentrations of solutions containing sodium, potassium, and calcium ions. The heart can adjust itself to other concentrations of the ions mentioned than the normal. The antagonistic action of calcium to potassium and to sodium is thought to be related to the atomic number of these elements, for whereas the difference of atomic number of potassium and calcium is unity, and their relative intensity is approximately equal, sodium has an atomic number nine less than calcium, and its antagonistic action is much less. H. K.

The Creatine Content of the Human Heart Muscle in Various Illnesses. FR. CONSTABEL (*Biochem. Z.*, 1921, **122**, 152—153).—Heart muscle in a braced condition contains a higher percentage of creatine than when in a relaxed condition as in fatty degeneration. H. K.

The Chemistry of the Lungs. I. UBALDO SAMMARTINO (*Biochem. Z.*, 1921, **124**, 234—243).—Lung tissue contains much cholesterol, cholesteryl esters, glyceryl palmitate, and unsaturated phosphatides. There is relatively little lecithin and kephalin, but a much larger proportion of cerebrosides and phosphosulphatides. H. K.

The Action of Pilocarpine on the Glycogen Content of Organs. URT HORNE MANN (*Biochem. Z.*, 1921, **122**, 269—273).—The hyperglycemia produced by pilocarpine was not influenced by administration of oxygen through the vena femoralis. The glycogen of the liver is used up, but that of the muscles shows but a slight decrease. H. K.

The Steric Transformation of the Hexoses through the Agency of Organs and Cells (the so-called Stereokinases). S. ISAAC and E. ADLER (*Z. physiol. Chem.*, 1921, 115, 105—129).—The surviving liver was the only organ which was found to be able to transform lævulose into dextrose. This organ fulfilled this function only when it was intact and irrigated. Other tissues, such as muscle or blood corpuscles, as well as the pulp and extracts of various organs failed to bring about this transformation.

S. S. Z.

Higher Alcohols in the Unsaponifiable Matter from Shark and Ray-fish Liver Oils. MITSUMARU TSUJIMOTO and YOSHIYUKI TOYAMA (*Chem. Umschau*, 1922, 29, 27—29, 35—37, 43—45).—Kagurazame oil (from the liver of *Hexanchus corinus*, Jordan and Gilbert) has the following characters: d_4^{20} 0.9146, acid number 0.49, saponification number 163.0, iodine number (Wijs) 124.5, n_D^{20} 1.4740, Hehner number 97.70, unsaponifiable matter 15.24%, glycerol 5.43%, acid number of the fatty acids 192.5, polybromide number of the fatty acids 26.30%. The oil does not contain squalene. The unsaponifiable matter consists chiefly of two new dihydric alcohols, one saturated and the other unsaturated. The saturated alcohol, *batyl alcohol*, $C_{10}H_{20}O_3$, is obtained by the hydrogenation of the unsaturated one in alcoholic solution at the ordinary temperature in the presence of platinum black. It crystallises in colourless, rectangular laminae with silvery lustre, m. p. 69°. The unsaturated *selachyl alcohol*, $C_{20}H_{40}O_3$, is a yellow liquid, d_4^{20} = 0.9206, n_D^{20} = 1.4690, iodine number 78.9. It is uncertain whether one of the three oxygen atoms of these alcohols is in the form of a hydroxyl group which cannot be acetylated or is part of an ether-like structure.

These alcohols also form the principal constituents of the unsaponifiable matter of the liver oils from the following species: *Cirrhigaleus barbifer*, *Somniosus microcephalus*, *Narcacion tokionis*, *Chimæra ovestoni*, *Chimæra mitsukurii*. They also occur together with large quantities of squalene in the unsaponifiable matter from the liver oils of *Lepidorhinus kimbei* and *Zamcus squamulosus*. The liver oil from *Chlamydoselachus anguineus* probably contains another alcohol as the principal constituent of the unsaponifiable matter. The principal constituent of the unsaponifiable matter of Doran-ci oil is cholesterol.

H. C. R.

The Stimulatory Action of Amino-acid Hydrochlorides on the Pancreatic Secretion. M. ARAI (*Biochem. Z.*, 1921, 121, 175—179).—The hydrochlorides of glycine, *d*-alanine, *d*-glutamic acid, and glycylglycine injected into the duodenum of a dog with a temporary pancreatic fistula cause a vigorous pancreatic secretion. Histidine hydrochloride and glucosamine hydrochloride had no action. Intravenous or subcutaneous administration of any of these salts was without result. Adrenaline inhibits such a pancreatic secretion, but atropine is without action.

H. K.

The Nucleic Acids of the Spleen of Cattle. H. STEUDEL (*Z. physiol. Chem.*, 1921, 114, 255—261).—As in the case of the

pancreas it is possible to obtain from the spleen of cattle guanilic acid and a real nucleic acid. The former was obtained from a protein isolated from the spleen by boiling the minced organ with water, filtering, and precipitating the filtrate with 50% acetic acid and alcohol. Guanilic acid was prepared from this protein by treating it with 2% sodium hydroxide on the water-bath, acidifying with acetic acid, and filtering. The guanilic acid separated from the filtrate on keeping. The nucleic acid was prepared from the residue of the spleen obtained after the aqueous extraction in the preparation of the protein by digesting it with 33% sodium hydroxide and precipitating with alcohol. Ten grams of the nucleic acid yielded 0.9 gram of guanine (calculated 0.8668) and 0.68 gram of adenine (calculated 0.7698). S. S. Z.

The Physiology of the Glands. XLVII. The Relations between the Thymus, Spleen, and Bone-marrow. LEON ASHER and GENGU MATSUMO (*Biochem. Z.*, 1921, **123**, 27—50).—The hæmoglobin and white corpuscular content of blood were examined after extirpation of the thymus and spleen. Stimulation of the bone-marrow of normal rabbits by hydrocyanic acid or by bleeding leads to a fall in the hæmoglobin, an increase of lymphocytes, but a decrease in the number of leucocytes. Extirpation of the thymus inhibits this response almost completely. Extirpation of the spleen, however, has little effect. H. K.

The Degradation of Carbohydrates in Transversely Striated Muscles. I. FRITZ LAQUER (*Z. physiol. Chem.*, 1921, **116**, 169—222).—The formation of lactic acid from various sugars by frog muscle has been studied under different physiological conditions. S. S. Z.

Reduction of the Aromatic Nitro-group as Indicator of Partial Processes of Respiration and of Fermentation. A Method for the Comparative Estimation of Biological Oxidoreduction. I. Experiments with Respiring Cells. II. Experiments with Fermenting Cells. W. LIPSCHITZ and A. GOTTSCHALK (*Pflüger's Archiv*, 1921, **191**, 1, 32—50; from *Physiol. Abstr.*, 1922, **6**, 589—590).—I. The *m*-nitrophenylhydroxylamine produced by the reducing action of tissues on *m*-dinitrobenzene can be estimated colorimetrically after filtration, and a quantitative measure of hydrogen activation thus obtained. Experiments on frog muscle show that the rate of reduction depends on the concentration of co-ferment in the sense in which that term was used by Meyerhof; the falling-off of the rate of reduction with time resembles that of the oxygen respiration rate. Reduction is destroyed by temperatures above 80°, is dependent on intact cell structure, is diminished with increase of oxygen pressure and by narcotics. Whilst combinations of narcotics have an additive effect on the reduction, a combination of a narcotic with hydrogen cyanide always shows less inhibition than the sum of the effects of the two substances separately, and not infrequently less than one alone. The curve relating inhibition to reduction of con-

centration of hydrogen cyanide is, unlike the oxygen respiration curve, a diphasic one, with a maximum at 0.05% and a new minimum at 0.5% potassium cyanide (neutralised). Reduction is lost after extraction of the muscle with water, but is restored again by muscle or yeast juice, or by succinic, fumaric, citric, glutamic, and α -glycerophosphoric acids; after partial extraction, it is restored to some extent by lactic acid, but never by maleic, glutaric, pyruvic, hydroxybutyric, or tartaric acid, or by glycerol, glyceric acid, dextrose, laevulose, or glycogen. In unextracted muscle reduction is accelerated by succinic and fumaric acids, but inhibited by maleic acid, also by saponin (cf. Hopkins, A., 1921, i, 635).

II. The musculatures of *Ascaris* and *Lumbricus* were studied as examples of facultative anaerobic tissues. *Ascaris* reduced powerfully; the reduction was independent of intact cell structure, was thermolabile, dependent on the presence of co-ferment, not inhibited by oxygen, and never inhibited more than 30% by hydrogen cyanide, the curve being also not diphasic. *Lumbricus* reduced less powerfully, the reduction being dependent on intact cell structure, and being inhibited up to 80% by hydrogen cyanide (uniphasic). The reduction by *Bacillus proteus* and *B. butyricus* is also (incompletely) inhibited by potassium cyanide (0.25%). E. S.

Fixation of Calcium by Animal Tissues. IV and V. E. FREUDENBERG and P. GYÖRGY (*Biochem. Z.*, 1921, 121, 131—141, 142—149).—IV. Natural cartilage rich in sodium, swells better than cartilage artificially enriched with calcium or magnesium. In all three cases there is a minimum of swelling at p_H 4.7, the isoelectric point of the cartilage protein.

V. Calcium is only taken up by cartilage at concentrations above 0.01N. Tryptic and autolytic processes, or the presence of urea, and ammonium chloride inhibit its fixation. H. K.

I. The Composition of Chinese Edible Birds' Nests and the Nature of their Proteins. II. The Isolation and the Nature of the Amino-sugar of Chinese Edible Birds' Nests. CHI CHE WANG (*J. Biol. Chem.*, 1921, 49, 429—439, 441—452).—The edible birds' nests contain a glucoprotein which is digested by both pepsin and trypsin. From the product of hydrolysis with hydrochloric acid a hexosamine hydrochloride was isolated which appears to be different from both glucosamine and chondrosamine hydrochlorides. It has $[\alpha]_D^{20}$ -70.6° (equilibrium), the initial rotation depending on the method of crystallisation, and becomes black at 250° after darkening at a much lower temperature. With phenylhydrazine and acetic acid, it forms an osazone which melts at 214° with rapid heating, and at a considerably lower temperature after remaining over sulphuric acid. The birds' nests contain inadequate protein for the growth of rats. E. S.

Bioluminescence. XIV. The Specificity of Luciferin and Luciferase. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1921, 4, 285—295).—The luciferin-luciferase reaction was obtained in a

few cases only out of a number of luminous organisms investigated. The luciferin of one species will not luminesce with the luciferase of another species unless closely related. Specificity is consequently indicated.

G. W. R.

The Identification of the Aldehyde-like Substance in the Urine of Diabetics as Acetaldehyde. W. STEPP and R. FEULGEN (*Z. physiol. Chem.*, 1921, **114**, 301—306).—The aldehyde-like substance in the urine of diabetic patients was concentrated by fractional distillation of the urine and was precipitated by dimethylcyclohexanedione as a substance of m. p. 138—140°. Comparison with ethyldenebisdimethylcyclohexanedione, prepared in similar manner from acetaldehyde, showed complete identity; it is therefore concluded that the volatile reducing substance found in the urine of some diabetics is acetaldehyde.

S. S. Z.

The Analytical Detection and Differentiation of Acetaldehyde, Aldol, Glyoxylic Acid, and their Presence in the Urine of Diabetic Patients. ROBERT FRICKE (*Z. physiol. Chem.*, 1921, **116**, 129—149).—Aldol forms a complex with "dimedon" [dimethyldihydroresorcinol] which can be differentiated from the analogous acetaldehyde complex by its insolubility in light petroleum. The presence of small quantities of crotonaldehyde was established in the urine in serious cases of diabetes. Furfuraldehyde and glyoxylic acid, on the other hand, were not found. The author confirms Stepp's observation concerning the presence of acetaldehyde in the urine of diabetic patients.

S. S. Z.

Excretion of Ammonia following Experimental Administration of Acids via the Stomach and Peripheral Vein. ROBERT W. KEETON (*J. Biol. Chem.*, 1921, **49**, 411—427).—Administration of hydrochloric acid to dogs by stomach tubes causes increased excretion of ammonia in the urine without affecting the total nitrogen excreted. If injected intravenously, however, there is an increased excretion both of ammonia and of total nitrogen.

E. S.

Creatine Formation in a Case of Progressive Pseudo-hypertrophic Muscular Dystrophy. R. B. GIBSON and FRANCES T. MARTIN (*J. Biol. Chem.*, 1921, **49**, 319—326).—In a case of this type ingested creatine was completely eliminated as creatine and creatinine, chiefly the former. The excretion of creatine and creatinine was increased by ingestion of protein and of glycocyamine, but was unaffected by sarcosine, asparagine, or cystine. The increase after administration of large amounts of protein was derived from the portion of the latter which was katabolised exogenously.

C. R. H.

First Results of the Treatment of Syphilis by Sodium *p*-Hydroxy-*m*-aminophenylarsinate or "189." L. FOURNIER, L. GUÉNOT, and A. SCHWARTZ (*Ann. Inst. Pasteur*, 1922, **36**, 53—62).—This salt, described by Fournieu (*ibid.*, 1921, **35**, 571) as No. 189, has a favourable action on human syphilis, although

it is not so powerful or constant in its results as salvarsan. It is relatively slightly toxic and is supported by patients who do not tolerate other arsenical preparations.

G. B.

Treatment of Syphilis by Bismuth. L. FOURNIER and L. GUÉNOT (*Ann. Inst. Pasteur*, 1922, 36, 14—33; cf. A., 1921, i, 908, and this vol., i, 89).—Sodium bismuthyl tartrate and other bismuth salts were administered, suspended in oil, by intramuscular injection (ten to twelve times 0.2—0.3 gram). Bismuth is an extremely powerful antisyphilitic agent; it is, however, apt to cause stomatitis. The bismuth is principally eliminated by the urine and, on keeping the latter, is deposited as sulphide as the result of a fermentative process.

G. B.

The Distribution Coefficients of Diuretics and Narcotics and the Theory of Narcosis. GIUSEPPE AIELLO (*Biochem. Z.*, 1921, 124, 192—205).—The distribution coefficients of caffeine, theobromine, ethoxycaffeine, and theophylline were determined between water and olive oil and between serum and olive oil. In each case the amount retained by serum is greater than that retained by water. The distribution coefficients of trional and sulphonal were determined between oil and serum. The failures of theories of narcosis is due to a lack of solvents exactly analogous to the tissue fluids concerned.

H. K.

Pharmacological Action of Colloidal Arsenious Sulphide. E. MENEGHETTI (*Biochem. Z.*, 1921, 121, 1—39).—Colloidal arsenious sulphide, in whatsoever way it is administered to rabbits, dogs, or guinea-pigs, changes its state of dispersion and becomes granular. When given intravenously, this may cause embolism of the lung capillaries, but if the animal survives, the after-effects are those of a metabolite, probably arsenious oxide.

H. K.

The Behaviour of Inactive Malic Acid in the Organisms of the Dog and Rabbit. M. TOMITA (*Biochem. Z.*, 1921, 123, 231—234).—Subcutaneous administration of *l*-malic acid to a rabbit resulted in the excretion of about 11% in the urine. When, however, the *dl*-malic acid was similarly administered to rabbits or dogs, the acid excreted was dextrorotatory.

H. K.

Barium Compounds in the Viscera. K. KRAFFT (*Z. Unters. Nahr. Genussm.*, 1921, 42, 390—391).—In a case of poisoning, a number of yellowish-white nodules were found adhering to the walls of the stomach. An analysis of these gave barium carbonate 64.7%, barium sulphate 35.3%. The quantity of barium remaining in the stomach was 0.2478 gram assuming equal distribution, but a large quantity had presumably been ejected by vomiting. Barium salts are converted into barium chloride in the stomach, with the exception of the insoluble barium sulphate. The minimum fatal dose of barium chloride is 0.09 gram per kilo of body-weight.

H. C. R.

Protein Intoxication. F. PENTIMALLI. **I. Introduction** (*Riforma med.*, 1921, 37, 532—536). **II. Toxicity of Egg-albumin and its Derivatives** (*Gazz. intern. med. chir. igiene*, 1921, 29, 65—72). **III. Toxicity of Peptones** (*Rass. intern. clin. terap.*, 1921, 2, 185—192). **IV. Toxicity of Milk and its Derivatives** (*La pediatria*, 1921, 29, 481—494). **V. Behaviour of Blood Pressure and of Respiration** (*Folia med.*, 1921, 7, 321—330). **VI. Behaviour of Body Temperature** (*Arch. sci. biol.*, 1921, 2, 44—58). **VII. Nystagmus** (*Riforma med.*, 1921, 27, 573—578). **VIII. Morphological Changes of the Blood** (*Hæmatologica*, 1921, 2, 527—578). (From *Physiol. Abstr.*, 1922, 6, 595—596.)—The physiological action of injections of proteins and protein products was studied under the various headings indicated in the titles. E. S.

Chemistry of Vegetable Physiology and Agriculture.

The Importance of Sequence in Biology. I. L. KARCZAG (*Biochem. Z.*, 1921, 122, 43—51).—Provided the number of bacteria used is not too large, the author shows that the addition of chloroform or toluene, first, to a dextrose bouillon and subsequent addition of *Bacillus coli*, has a greater inhibiting influence than the addition of *B. coli* to a dextrose bouillon, first, and then addition of the antiseptic. In both cases there is inhibition compared with the control. H. K.

The Importance of Sequence in Biology. II. L. KARCZAG and K. HAJÓS (*Biochem. Z.*, 1921, 122, 52—57).—That the order of mixing the components is of influence, the authors show by a study of the systems (a) the antitryptic action of serum (trypsin+casein+serum), (b) the hæmolytic system (corpuscles+complement+hæmolysin), (c) the bacteriolytic action of immune serum on *Paratyphosus-B* (Pfeiffer's experiment). H. K.

The Importance of the Amino-acids of Hæmoglobin for the Cultivation of the Influenza Bacilli. MARTIN JACOBY and KÄTE FRANKENTHAL (*Biochem. Z.*, 1921, 122, 100—104).—The influenza bacillus can be caused to grow on agar if histidine be added. A less favourable growth is obtained on addition of leucine. H. K.

The Degradation of *l*-Tryptophan by *Bacillus proteus*. TAKAOKI SASAKI and ICHIRO ÔTSUKA (*Biochem. Z.*, 1921, 121, 167—170).—*l*-Tryptophan, in a suitable medium containing glycerol is converted by *B. proteus* into *l*-indole-lactic acid. The isolation of this acid is simplified by its quantitative precipitation by basic copper acetate solution. H. K.

The Degradation of *dl*- α -Naphthylalanine by *Bacillus proteus*. TAKAOKI SASAKI and JIRO KINOSE (*Biochem. Z.*, 1921, 121, 171—174).—Glycine anhydride when condensed with α -naphth-aldehyde by Sasaki's reaction gives 2:5-diketo-3:6-dinaphthyl-idene-piperazine, unmolten at 320°. Reduction with hydriodic acid and red phosphorus leads to *dl*- α -naphthylalanine, m. p. 240°. On submitting the latter amino-acid to the action of *B. proteus*, *d*-naphthylalanine was isolated, m. p. 142° (corr.) and $[\alpha]_D^{25} + 24.31^\circ$ in alcohol. H. K.

The Bacterial Degradation of *l*-Leucine. MINORU ARAI (*Biochem. Z.*, 1921, 122, 251—257).—*l*-Leucine submitted to *Proteus vulgaris* on a suitable medium gave the corresponding nitrogen-free *d*-hydroxy-acid, but *Bacillus subtilis* gave the levo-acid. By varying the nutrient medium, *P. vulgaris* gave isoamyl-amine. H. K.

Influence of the Hydrogen-ion Concentration on the Growth and Formation of Toxin of Tetanus Bacilli. K. G. DERNBY and B. ALLANDER (*Biochem. Z.*, 1921, 123, 245—271).—Growth of tetanus bacilli takes place between P_H 5 and 8.5, the optimum range being between 7 and 7.6. The stability zone, however, of tetanus toxin is between P_H 5.8 and 8, the optimum range being 6.0 to 7.5. For large-scale preparation of tetanus toxin, the initial P_H should be 8 and when more acidity develops than P_H 6.8, fresh neutralisation is necessary. H. K.

Microchemistry of a New Group of Purple Bacteria. JOS. GICKLHORN (*Ber. Deut. bot. Ges.*, 1921, 39, 312—319).—Two new species of purple bacteria, namely, *Chromatium Linsbaueri* and *Rhabdochromatium Linsbaueri*, are shown to contain, in addition to sulphur, considerable quantities of amorphous calcium carbonate. G. W. R.

The Oxidation of Sulphur by Soil Organisms. JACOB G. LIPMAN, SELMAN A. WAKSMAN, and JACOB S. JOFFE (*Soil. Sci.*, 1921, 12, 475—490).—A study of the chemical changes occurring during the growth of *Thiobacillus thio-oxidans* in artificial media is reported. The hydrogen-ion concentration and titratable acidity of the medium increase with the age of the culture, as also does the amount of sulphate produced. There appears to be a period of marked activity after four and again after eight days. Sulphate production is followed by the conversion of insoluble into soluble phosphates; 94% of the total insoluble phosphate was rendered soluble in fifteen days, but no further increases occurred. Old cultures (one hundred and twenty days) were found to have P_H 0.8 and their acidity was 0.68N. Optimum growth of the organism occurs in media with P_H 2.8—2.0, although the organism can exist in a medium of P_H 0.58. Acidity less than that corresponding with P_H 5.6 is unfavourable. The possible uses of sulphur manuring to combat potato scab, to reclaim black alkali soils, and increase the availability of phosphates and potassium, are indicated. A. G. P.

The Formation of Acetaldehyde and the Realisation of the Second Form of Fermentation with Various Fungi. CARL NEUBERG and CLARA COHEN (*Biochem. Z.*, 1921, **122**, 204—224).—A large number of micro-organisms can ferment dextrose with production of acetaldehyde and glycerol. The acetaldehyde was fixed by addition of sodium hydrogen sulphite or calcium sulphite. When the proportion of acetaldehyde was large, the production of an equivalent proportion of glycerol was demonstrated.

H. K.

A Biological Method for the Estimation of Substances which Injure the Cell and the Embryo. II. ALFRED SCHNABEL (*Biochem. Z.*, 1921, **122**, 295—300; cf. A., 1921, ii, 788).—A graphic modification of the author's previously described method for determining the concentration of substances which inhibit the methylene-blue reducing capacity of bacteria.

H. K.

Comparative Experiments on the Antiseptic Action of some Chloro-derivatives of Methane, Ethane, and Ethylene. GEORG JOACHIMOGLU (*Biochem. Z.*, 1921, **124**, 130—136).—The antiseptic action of aqueous solutions of chloro-derivatives of methane, ethane, and ethylene on *Vibrio Metschnikoff* falls off in the order hexachloroethane, tetrachloroethylene, pentachloroethane, tetrachloromethane, trichloroethylene, dichloroethylene, $\alpha\alpha$ -dichloroethane, tetrachloroethane, $\alpha\beta$ -dichloroethane, chloroform, dichloromethane.

H. K.

Bactericidal Action of Pyromucic Acid. H. P. KAUFMANN (*Ber.*, 1922, **55**, [B], 289—290).—Pyromucic acid in 0.5% and 1% solution kills *Bacillus coli* within five minutes, in 0.25% solution within thirty minutes, and in 0.1% solution within seven hours; development is arrested in 0.05% solutions. *Staphylococcus aureus* is rather more resistant to pyromucic acid. The salts of the latter have only slight bactericidal action. In its effect, pyromucic acid is very similar to benzoic acid, but the latter is much superior in practical application to products such as fruit and meat.

H. W.

Nature of Yeast Fats. IDA SMEDLEY MACLEAN (*Z. physiol. Chem.*, 1921, **113**, 199—200).—Polemical. A reply to Hinsberg and Roos (A., 1921, i, 148).

S. S. Z.

Yeast Gum and Saccharase. E. SALKOWSKI (*Z. physiol. Chem.*, 1921, **114**, 307—308).—A reply to Svanberg (A., 1921, i, 202). Saccharase is not always associated with gum in yeast.

S. S. Z.

The Nitrogenous Constituents of Yeast. II. The Purine Bases and the Diamino-acids. Results. JACOB MEISENHEIMER (*Z. physiol. Chem.*, 1921, **114**, 205—249).—Top and bottom fermentation yeasts show no marked differences in the composition of their products of degradation. Ammonia forms 8% of the total nitrogen. Twelve per cent. of the total nitrogen can be

accounted for in the purine and pyrimidine bases as follows: guanine 4%, adenine 4%, cytosine (?) 2.4%, and uracil (?) 1.6%. Ten per cent. is present as histidine and arginine, and 10% as lysine. Of the 60% of the total nitrogen found to be associated with the monoamino-acids, 0.5% was traced to glycine, 10–15% to alanine, 10–15% to valine, 5–10% to leucine, 2% to proline, 8% to phenylalanine, 3.5% to aspartic acid, 6% to glutamic acid, 2% to tyrosine, 0.5% to tryptophan, 2% to cystine and other sulphur compounds, 4.5% to oxyproline (?), 0.5% to choline, and 0.5% to glucosamine. The ratio of amino- to nonamino-nitrogen as obtained by Van Slyke's method was always found to be lower than the figures calculated from the above data. S. S. Z.

The Nitrogenous Constituents of Yeast. MARTIN SCHENCK (*Z. physiol. Chem.*, 1921, **116**, 308–309).—Polemical, in reply to Meisenheimer (*A.*, 1919, i, 370; preceding abstract). S. S. Z.

Carboligase. II. CARL NEUBERG and LUDWIG LIEBERMANN (*Biochem. Z.*, 1921, **121**, 311–325; cf. *A.*, 1921, i, 480).—*o*-Chlorobenzaldehyde was added to yeast undergoing fermentation. *o*-Chlorobenzyl alcohol and *o*-chlorobenzoic acid were isolated. The enzyme carboligase causes a condensation of another portion of the aldehyde with acetaldehyde with formation of the ketone-alcohol, $C_6H_4Cl\cdot CH(OH)\cdot C(OMe)_2$, which exhibits optical activity but gives an inactive *p*-nitrophenyllosazone, m. p. 302–303°, *thiosemicarbazone*, m. p. 216–218°. Anisaldehyde reacts less smoothly. The *p*-nitrophenyllosazone of the corresponding ketone-alcohol was isolated, m. p. 266°. The ketone alcohols will be described later. H. K.

The Thermostability of the Co-enzyme and its Separation from Vitamin-B from Yeast. TH. THOMAS (*Z. physiol. Chem.*, 1921, **115**, 235–256).—One half of the co-enzyme of alcoholic fermentation is destroyed by heating at 96° for one hour, or at 100° for thirty-seven minutes at P_{II} 5.6. The vitamins from yeast and cabbage which accelerate alcoholic fermentation differ in their thermostability from the co-enzyme and are therefore not identical with it. It is thus possible to separate the two substances. S. S. Z.

The Dismutation of Various Aldehydes by Yeast. H. KUMAGAWA (*Biochem. Z.*, 1921, **123**, 225–230).—*iso*Valeraldehyde, *isobutyl*aldehyde, heptaldehyde, and benzaldehyde when submitted to the action of yeast in a 1% sodium hydrogen carbonate solution undergo the Cannizzaro reaction and yield the corresponding acids and alcohols. The proportion of the alcohol is usually somewhat greater than that of the acid, owing to a simultaneous phytochemical reduction of the original aldehyde. H. K.

The Course of Alcoholic Fermentation in Presence of Calcium Carbonate. JOHANNES KERB and KURT ZECKENDORF (*Biochem. Z.*, 1921, **122**, 307–314).—The authors are unable to confirm the experiments of Fernbach and Schoen (*A.*, 1920, i, 406)

on the production of considerable quantities of pyruvic acid by fermentation in presence of calcium carbonate. Its production in Fernbach and Schoen's experiments must be as a by-product due to oxidation of lactic acid by use of an atypical yeast.

H. K.

Pyruvic Acid as an Intermediary in the Alcoholic Fission of Dextrose. MAX VON GRAB (*Biochem. Z.*, 1921, **123**, 69—89).—Apart from the experiments of Fernbach and Schoen (*A.*, 1920, i, 406) with an atypical yeast, pyruvic acid has never been isolated as an intermediate product in a typical yeast fermentation. By use of a new fixative, β -naphthylamine, the author has isolated the condensation product of pyruvic acid and β -naphthylamine—namely, α -methyl- β -naphthacinchonic acid—from the interaction of press juice and dextrose.

H. K.

The Enzymic Synthesis of Fructosediphosphate (Hexose-phosphate). HANS V. EULER and FOLKE NORDLUND (*Z. physiol. Chem.*, 1921, **116**, 229—244).—The optimum H-ion concentration for the formation of fructose diphosphate by a bottom fermentation yeast was found to be P_H 6.2—6.6. This reaction is about the optimum for all sugars; levulose, however, showed a somewhat different reaction curve.

S. S. Z.

Maltase. IV. The Fermenting Activity of Yeasts Poor in Maltase. RICHARD WILSTÄTTER and WERNER STEIBELT (*Z. physiol. Chem.*, 1921, **115**, 211—234; cf. this vol., i, 282).—The approximate figure for the quotient (time value for maltase/time value for saccharase) for brewer's yeasts was found to be 20. The time values for saccharase in the brewer's yeast strains did not show great variations; on the other hand, those in some of the distiller's yeast strains differed within very wide limits, as also did the time values for maltase in the different strains. The fermenting capacity of the various yeasts was studied. From the observations made it was concluded that maltose can also be fermented without being previously hydrolysed, as the hydrolysis by some strains proceeded much more slowly than the actual fermentation by those strains. No dextrose could be established in the fermenting medium when the fermentation of maltose carried out with maltase-free yeasts was interrupted.

S. S. Z.

The Action of Salts on the Bleaching of Methylene-blue by Various Species of Yeast. H. KUMAGAWA (*Biochem. Z.*, 1921, **121**, 150—163).—The reducing capacity of various species of yeast for methylene-blue is very variable. Metallic salts inhibit or retard the reduction, but not invariably. The somewhat anomalous results are attributed to the influence of the physiological state of the yeast-cells at the moment of the experiment.

H. K.

New Classes of Stimulants of Alcoholic Sugar-fission. VII. CARL NEUBERG, ELSA REINFURTH, and MARTA SANDBERG (*Biochem. Z.*, 1921, **121**, 215—234).—A large number of purine derivatives have been tested and found without exception to have a stimulating

effect on the process of cell-free fermentation of dextrose by means of yeast press juice. The nucleosides adenosine and guanosine were also beneficial and the nucleic acids to a lesser extent. Degradation products of purines had a distinctly favourable influence. The authors hesitate to class the above substances as hydrogen acceptors. H. K.

The Action of Silver Compounds on Yeast. ERNEST ZERNER and ROBERT HAMBURGER (*Biochem. Z.*, 1921, **122**, 315—318).—Silver nitrate, chloride, and carbonate have a toxic action on yeast. H. K.

Nature of Alcoholic Fermentation. C. C. WARDEN (*Amer. J. Physiol.*, 1921, **57**, 454—469; from *Physiol. Abstr.*, 1922, **6**, 600).—The conclusion is drawn from experiments described, more especially as to the effect of the addition of surfaces of various kinds, that alcoholic fermentation is a catalytic process occurring at the surface of yeast-cells, on the colloidal surfaces of yeast juice, and at artificial surfaces composed of fat complexes similar to those found in yeast-cells. Further, it is held that the enzyme of yeast belongs to the cellular antigens. Interesting considerations as to the nature of enzyme action on anti- and co-enzymes will be found in the paper. E. S.

The Decomposition of *d*-Galactose according to the Second Mode of Fermentation. M. TOMITA (*Biochem. Z.*, 1921, **121**, 164—166).—*d*-Galactose, like *d*-glucose, *d*-mannose, and *d*-fructose, when fermented in the presence of disodium sulphite gives an equimolecular proportion of acetaldehyde and glycerol. H. K.

Fermentation without Yeast. A. BAU (*Biochem. Z.*, 1921, **122**, 303—306).—A criticism of the claims of Baur and Herzfeld (*A.*, 1922, i, 93). H. K.

Photosynthesis and the Functions of Pigments in the Living Plant. E. C. C. BALY (*J. Soc. Dyers and Col.*, 1922, **38**, 4—9).—The author deals with photochemical reactions, and, in particular, the conversion of carbon dioxide and water into formaldehyde and oxygen as the first step in the synthetic growth of the vegetable organism. In the laboratory, the oxygen tends to oxidise the formaldehyde to formic acid, but in the living plant it is quantitatively evolved as oxygen. Suggestions as to the mechanism whereby gaseous oxygen is transpired are outlined. F. M. R.

Photosynthesis. I. The Ratio of Carbon Dioxide to Oxygen in Carbon Assimilation. S. KOSTYTSHEV (*Ber. Deut. bot. Ges.*, 1921, **39**, 319—328).—The ratio CO_2/O_2 may depart from unity in the case of leaves exposed to artificial atmospheres containing abnormally large amounts of carbon dioxide. The assimilation of carbon dioxide is at first in excess of the oxygen liberated, but after a short time this relation is reversed. Eventually the ratio becomes normal. Similar results are obtained with algae. It is unlikely that under normal conditions variations

in the ratio of carbon dioxide absorbed to oxygen liberated occur. Assimilation should be measured by the amount of carbon dioxide absorbed, and not by the amount of oxygen liberated. G. W. R.

Photosynthesis. II. Does Injury Stimulate Photosynthesis? S. KOSTYTSHEV (*Ber. Deut. bot. Ges.*, 1921, 39, 328—333).—Injury to leaves was found to be without any stimulating effect on carbon assimilation. A slight depression of assimilation observed was attributed to restriction of the assimilating area consequent on the method of experiment. G. W. R.

Photosynthesis. III. Does Carbon Assimilation take place during Summer Night in Subarctic Regions? S. KOSTYTSHEV (*Ber. Deut. bot. Ges.*, 1921, 39, 334—338).—Carbon assimilation generally ceases at sunset, even although the twilight in latitude 60° N. furnishes sufficient light for the process to go on. This may be due to the effect of the fall in temperature in closing the stomata. A certain amount of carbon assimilation was found to take place after sunset in the case of coniferous trees. G. W. R.

The Chemical Constitution of Protoplasm. HEINRICH WALTER (*Biochem. Z.*, 1921, 122, 86—99).—The protoplasm of myxomycetes behaves like that of the higher plants. When extracted from the cells with absolute alcohol, ether, and chloroform, it is only partly digested by pepsin, but completely by trypsin. The plasma consists of a phospho-protein-like substance, plastin, which is digested by trypsin, and a lipid component. H. K.

Direct and Indirect Determinations of Permeability. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1921, 4, 275—283).—A method is described for determining the electrical conductivity of the cell sap of a species of *Nitella*. The results obtained by tests of the sap isolated from cells show that, whilst in pure sodium nitrate solution rapid penetration of the nitrate ion takes place accompanied by injury to the cell, in the case of a balanced solution of calcium nitrate and sodium nitrate penetration is slow and the cell remains uninjured. Direct evidence was obtained for the supposition that both penetration and also recovery from plasmolysis are more rapid in the case of injurious solutions than in the case of non-toxic solutions. G. W. R.

Penetration of Kations into Living Cells. MATILDA MOLDENHAUER BROOKS (*J. Gen. Physiol.*, 1921, 4, 347—349).—The permeability of the protoplasm of a species of *Nitella* was investigated by examination of the cell sap. The protoplasm is normally permeable to lithium, caesium, and strontium ions, penetration being more rapid in unbalanced than in balanced solutions. G. W. R.

The Permeability of Plant-plasma for Neutral Salts. IV. HUGO КАМНО (*Biochem. Z.*, 1921, 123, 284—303; cf. A., 1922, i, 94).—Micrometer observations were made on the first root of yellow

lupin (1 to 1.5 cm. long) when placed in isotonic salt solutions, which were, however, hypertonic to the plant plasma. The initial contraction is followed by a relatively slower and smaller expansion. This latter is used as a measure of the penetrability of various salts. The permeability of the ions follows the sequence $\text{NO}_3, \text{I}, \text{Br} > \text{Cl} > \text{tartrate} > \text{SO}_4 > \text{citrate}$ and $\text{K} > \text{Na} > \text{Li} > \text{Mg} > \text{Ba} > \text{Ca}$. Moreover, the permeability of an ion is inhibited by a second ion the further it lies to the right in this series. The results accord with the view that the toxicity of neutral salts stands in close relation to the permeability of plasma for these salts.

H. K.

The Green Respiratory Pigment and its Importance in the Oxidation of Protein Substances in the Sprouting Seeds of *Helianthus annuus*. ALEXANDER OPARIN (*Biochem. Z.*, 1921, 124, 90—96).—Cortier's chlorogenic acid absorbs two molecules of oxygen in alkaline solution. Analysis points to a removal of four atoms of hydrogen by the oxygen. This formation of a green oxidation product is accelerated twenty-fold by addition of phenolase from sunflower seeds. Experiments were carried out on the oxidation of amino-acids, peptides, and proteins in the presence of chlorogenic acid, use being chiefly made of the Van Slyke methods of analysis. The results are held to support the view that the amino-acids and proteins become oxidised with liberation of ammonia. In the living plant, the latter is used for the synthesis of asparagine and glutamine.

H. K.

Effect of Transpiration on the Disappearance of Starch from Leaves. HANS MOLISCH (*Ber. Deut. bot. Ges.*, 1921, 39, 333—344).—The disappearance of starch from leaves placed in darkness is more rapid in a dry than in a moist atmosphere. Leaves kept in a moist atmosphere, although little of their starch had been altered, contained more reducing sugars than leaves kept in a dry atmosphere which had lost all their starch. It is supposed that substances other than sugars, probably dextrans and similar substances, are formed from the decomposition of starch. It is not necessary to assume translocation, as the starch reaction disappears even in stalkless leaves.

G. W. R.

The Oxalic Acid Content of Early Spring Leaves, and some Observations concerning this Acid. A. BAV (*Z. tech. Biol.*, 1921, 8, 151—155; from *Physiol. Abstr.*, 1922, 6, 599).—Oxalic acid was found in the young leaves of elder, hawthorn, and horse-chestnut, and in those of young barley plants.

E. S.

The Manganese Content of Flowers. D. H. WESTER (*Pharm. Weekblad*, 1922, 59, 51—55).—Various carefully selected flowers were gathered from dry dust-free localities in dry weather, and transferred at once to closed tared flasks. Moisture, ash, and manganese were determined in the samples. The average moisture content was between 80 and 90% (minimum 75.6, maximum 94.5%). Ash averaged 1% (minimum 0.31%, maximum 1.93%). All species examined contained manganese, varying from 11.2 to 222.1 mg.

per 100 grams of ash, but no regularity was observed in its distribution between families. Only small differences were observed between individuals of the same species plucked at different times and places.

S. I. L.

The Occurrence of Calcium Oxalate in the Gidgee Wattle (*Acacia cambagei*, Baker). THOS. STEEL (*Chem. News*, 1921, **123**, 315—316).—Both the outer and inner bark of *A. cambagei* contain 18.82% of calcium oxalate, calculated as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ on the dry weight, whilst the outer white wood contains 5.81% and the inner dark wood 3.81%. Samples of bark from other species of *Acacia* contained amounts varying from 1.36 to 8.92% of the oxalate.

W. G.

Chemical Constituents of a Chinese Drug "Hsiung Ch'uang." I. YOSHIHARU MURAYAMA (*J. Pharm. Soc. Japan*, 1921, No. 477, 951—959).—From a Chinese drug "Hsiung Ch'uang" or "Ch'uang Hsiang," the dried root of *Cnidium officinale*, Makino, Sakai (*Tokyo Igakukai Zasshi*, 1916, 935) isolated a phenol; an ester, $\text{C}_{22}\text{H}_{36}\text{O}_3$ (which when saponified gave enidic acid, $\text{C}_{12}\text{H}_{20}\text{O}_3$, and an alcohol, $\text{C}_{10}\text{H}_{18}\text{O}$), and enidiolactone, $\text{C}_{12}\text{H}_{18}\text{O}_2$, b. p. 177—178°/15 mm. By distilling the powdered drug with steam and extracting with ether, the author has obtained a brownish-yellow, viscous oil of characteristic odour, from which *cnidiolactone*, $\text{C}_{12}\text{H}_{18}\text{O}_2$, was separated as an oil, b. p. 178—180°/13 mm., $d_{20} 1.047$, $n_D^{20} -65.0^\circ$, $n_D^{25} 1.5061$. By reduction with sodium and alcohol, followed by treatment with 1% potassium permanganate, the lactone gave a compound, $\text{C}_{12}\text{H}_{22}\text{O}_3$, crystallising in white needles, m. p. 50°, which seems to be *dihydrocnidic acid*. By reduction with hydrogen in the presence of platinum black, the lactone gave *cnidic acid*, $\text{OH} \cdot \text{C}_{11}\text{H}_{18} \cdot \text{CO}_2\text{H}$, m. p. 87°, which is unstable and is readily converted into the dihydro-acid. When oxidised with potassium permanganate, the lactone yields phthalic and valeric acids, and therefore would appear to be an isomeride of the lactone, sedanolide, obtained by Ciamician and Silber from oil of celery (*A.*, 1897, i, 484).

K. K.

The Chemical Constituents of Green Plants. XIV. The Acids in the Currant (*Ribes rubrum*) which are Precipitated by Lead Acetate. HARTWIG FRANZEN and EUGEN SCHUMACHER (*Z. physiol. Chem.*, 1921, **115**, 9—37).—The currant contains large quantities of citric acid, and small amounts of malic acid. The former is about forty-seven times the amount of the latter. Tartaric acid is only present as traces. Acids which yield esters with a higher boiling point than triethyl citrate and are precipitated by lead acetate, are also present in very small amounts.

S. S. Z.

The Chemical Constituents of Plants. XVII. The Presence of Lactic Acid in the Leaves of the Blackberry (*Rubus fruticosus*). HARTWIG FRANZEN and ERNST KEYSSNER (*Z. physiol. Chem.*, 1921, **116**, 106—108).—The presence of lactic acid was established in the leaves of the blackberry.

S. S. Z.

The Chemical Constituents of Green Plants. XV. The Presence of Lactic Acid in the Leaves of the Raspberry (*Rubus idaeus*). HARTWIG FRANZEN and EMMI HERN (*Z. physiol. Chem.*, 1921, **115**, 270—283).—The leaves of the raspberry contain lactic acid. The presence of lactic acid was also established in the opium poppy (*Papaver somniferum*), germinated castor oil seed (*Ricinus communis*), and in the leaves of *Agave Sisalana*.

S. S. Z.

I. Culture Experiments with Soja Beans. II. Occurrence of Urease in Parts of the Plant Other than the Seeds. D. H. WESTER (*Biochem. Z.*, 1921, **122**, 188—192).—Attempts to cultivate soja beans in Holland were unsuccessful. Urease was found in various portions of the plant other than the seeds.

H. K.

Botanical Chemical Observations. EDMUND O. VON LIEPMANN (*Ber.*, 1921, **54**, 3111—3114).—In an isolated case, mannose has been obtained from the fruit of *Symphoricarpos racemosus*; subsequent attempts to repeat the isolation led invariably to the production of dextrose.

A lemon-yellow deposit on the leaves of the ordinary white anemone, collected after a protracted spell of warm weather, was identified as calcium succinate.

The roots of the ordinary reed, collected in early summer, generally contained about 1—3% of sucrose, but occasionally 3—3.5%. This figure is somewhat lower than that recorded recently by Sabalitschka for roots collected in November.

A voluminous black powder found in the hollow of a felled oak became spontaneously heated when spread in a thin layer in bright sunlight, and then contained a considerable proportion of mellitic acid, which, however, was not present in the original specimen.

H. W.

Application of the Biochemical Method for Characterising Dextrose to the Fruits of *Viburnum opulus* and to Extracts of Red *Cinchona* and of Cola. R. ARNOLD (*Bull. Soc. Chim. Biol.*, 1921, **3**, 547—566).—The principle of the method is the synthetic action of emulsin on a solution of dextrose in 50% methyl alcohol, measured by a fall in the reducing power; in all the cases referred to, β -methylglucoside was obtained crystalline. If reducing substances other than sugar are present, it is not enough to extract the material simply with boiling alcohol. The extract must then be purified by basic lead acetate, and impurities must be extracted with wet boiling ethyl acetate. The sugars are then extracted by boiling 95% alcohol. In most fruit, about half the reducing sugar is dextrose, that is, it contains invert-sugar. In extract of Cola nuts only 21.7% of the reducing substances is dextrose, but after hydrolysis by acid it is 48.8%.

G. B.

The Toxic Action of Heavy-metal Salts on Plant Plasma. III. HUGO KAHHO (*Biochem. Z.*, 1921, **122**, 39—42; cf. this vol., i, 94).—The toxicity of various kations of the heavy metals

on plant plasma was investigated. The order followed is approximately that of the electrolytic solution pressure of these cations. Zincion is the most noticeable exception, its toxicity approaching that of copper.

H. K.

The Influence of certain Factors on the Chemical Composition of Sauerkraut. O. R. BRUNKOW, W. H. PETERSON, and E. B. FRED (*J. Amer. Chem. Soc.*, 1921, **43**, 2244—2255).—Inoculation with certain organisms produced a better grade of sauerkraut than is produced by a natural fermentation, but the only organism consistently better than the control was *Bacillus lactis acidi*. The presence of a large number of yeasts may result in a red kraut with undesirable flavour. The concentration of salt in the brine is of importance. The best kraut was obtained when 2% of salt was used, and with concentrations above 3% the kraut was tough and too salt.

The chief products in the fermentation of kraut are lactic acid, acetic acid, and ethyl alcohol. Mannitol may also be produced in varying amounts, depending on the type of organisms present. The relative amounts of these various products can be influenced by inoculation.

W. G.

The Diastatic Action of Malt and its Preparations (Liquid, Syrupy, and Dried Extracts). RAOUL LECOQ (*J. Pharm. Chim.*, 1922, **25**, 18—25).—The diastatic action of malt is practically limited to the temperature range 60—90°. The activity is greatest between 70° and 80°, with an optimum at about 75°. Mixed in sufficient quantity, namely, about 30%, with cooked or uncooked barley flour, saccharification takes place with an approximately corresponding velocity in the temperature range 60—80°, and likewise with an optimum at 75°. The activity of malt itself is three to four times greater than that of any of the extracts prepared commercially from it. The latter consist largely of maltose, the diastase being to a great extent destroyed in the process of manufacture.

G. F. M.

The Sulphur-oxidising Power of Soils. A. DEMOLON (*Compt. rend.*, 1921, **173**, 1408—1410; cf. A., 1912, ii, 382; 1913, i, 579).—By growth on sand cultures containing free sulphur admixed with the sand, oxidation of the sulphur to sulphate by bacterial extracts from soils was obtained. Soils vary considerably in their sulphur-oxidising power, garden soils rich in organic matter giving the best results. The presence of calcium carbonate is only necessary if there is insufficient carbamide present to supply the ammonia necessary to keep the medium neutral. The ammonifying organisms in the soil are apparently responsible for sulphur oxidation, and the property is not bacteriologically specific.

W. G.

Organic Chemistry.

The Composition of Paraffin Wax. I. FRANCIS FRANCIS [with JOHN CLIFFORD POPE and REGINALD HENRY COYSH] (*T.*, 1922, **121**, 496—513).

Synthesis of Trimethylethylmethane [$\beta\beta$ -Dimethylbutane]. (Mlle.) H. VAN RISSEGHEN (*Bull. Soc. chim. Belg.*, 1922, **31**, 62—66; cf. van Risseghem, A., 1921, i, 489, and Markownikow, A., 1899, i, 534).—The preparation of $\beta\beta$ -dimethylbutane from pinacone is carried out by transforming it into pinacolin, which is then treated with phosphorus pentachloride. The resulting product is a mixture of $\beta\beta$ -dichloro- $\gamma\gamma$ -dimethylbutane, a solid, and the unsaturated derivative, $\text{CMe}_2\text{CCl}:\text{CH}_2$, a liquid. The latter is heated with potassium hydroxide in sealed tubes and the product, dimethylbutinene, distilled off. This is treated with hydrogen in presence of platinum black, the resulting hexane is washed, dried over calcium chloride, and distilled.

The following physical constants have been determined: $\beta\beta$ -dimethylbutane, m. p. -98.2° , d_4^{20} 0.6678, d_4^{15} 0.6538, n_D^{16} 1.36972, n_D^{15} 1.37158, n_H^{15} 1.37615, $n_{H\gamma}^{15}$ 1.37964; isohexane, n_D^{15} 1.37257, n_D^{16} 1.37445, $n_{H\beta}^{15}$ 1.37914, $n_{H\gamma}^{15}$ 1.38251; γ -methylpentane, n_D^{15} 1.37753, n_D^{16} 1.37929, $n_{H\beta}^{15}$ 1.38404, $n_{H\gamma}^{15}$ 1.38740; $\beta\gamma$ -dimethylbutane, n_D^{15} 1.37905, n_D^{16} 1.38092, $n_{H\beta}^{15}$ 1.38540, $n_{H\gamma}^{15}$ 1.38893; dimethylbutinene, m. p. -81.2° , d_4^{20} 0.6899, d_4^{15} 0.6737, n_D^{15} 1.37518, n_D^{16} 1.37725, $n_{H\beta}^{15}$ 1.38313.

H. J. E.

Tetrapropylethane [$\delta\epsilon$ -Dipropyloctane]. JEAN PICCARD and RAY Q. BREWSTER (*J. Amer. Chem. Soc.*, 1921, **43**, 2626—2629).—When butyrene is reduced with metallic sodium in the presence of a little ether, the products are δ -hydroxyheptane and some $\delta\epsilon$ -dipropyloctane- $\delta\epsilon$ -diol. The hydroxyheptane gives, with phosphorus and iodine, δ -iodoheptane, and this, when treated with sodium in absolute ether, gives *s*-tetrapropylethane [$\delta\epsilon$ -dipropyloctane], $\text{CHPr}_2\text{CHPr}_2$, b. p. $105\text{--}106^\circ/12\text{ mm.}$, or $220^\circ/760\text{ mm.}$: d_4^{20} 0.7735; n_D^{20} 1.4322; surface tension 25.64 dynes/cm. An identical dipropyloctane was obtained by heating the dipropyloctanediol with concentrated hydriodic acid in a sealed tube at 180° for ten hours.

W. G.

Action of Polyhalogenated Compounds of Methane and Ethane on Magnesyl [Magnesium Alkyl] Compounds. B. ODDO and R. BINAGHI (*Gazzetta*, 1921, **51**, ii, 330—337).—The action of iodoform on magnesium phenyl bromide yields principally tetraphenylethane, together with iodobenzene, formed from the intermediate α -iododiphenylmethane, and diphenyl.

The products of the interaction of iodoform and magnesium ethyl bromide are acetylene, ethane, methane, ethyl bromide and

iodide, traces of methyl iodide and di-iodomethane, and an unknown compound with an acute odour recalling that of marine algæ.
T. H. P.

Symmetrical Di-iodoethylenes. G. LATIERS (*Bull. Soc. chim. Belg.*, 1922, **31**, 73—84; cf. Chavanne and Vos, A., 1914, i, 796).—A study from the kinetic point of view of the spontaneous transformation of the two stereoisomeric di-iodoethylenes into each other until equilibrium is reached.
H. J. E.

New Synthesis of Primary Alcohols, and Constitution of Hydrogen Peroxide. B. ODDO and R. BINAGHI (*Gazzetta*, 1921, **51**, ii, 343—348).—When cooled in a mixture of ice and salt, hydrogen peroxide solution and magnesium alkyl haloids interact with formation of primary alcohols: $\text{CH}_3\text{R} \cdot \text{MgX} + \text{H}_2\text{O}_2 = \text{CH}_3\text{R} \cdot \text{OH} + \text{MgX} \cdot \text{OH}$; the decomposition of the magnesium complex by the water present in the peroxide in accordance with the equation $\text{CH}_3\text{R} \cdot \text{MgX} + \text{H}_2\text{O} = \text{MgX} \cdot \text{OH} + \text{R} \cdot \text{CH}_3$, takes place only slowly. The formation of alcohol is not direct, but results from the decomposition of an intermediate additive compound which forms characteristic, yellowish-white globules and floats on the ethereal solution.

These results are discussed in relation to the possible constitutions for hydrogen peroxide, and it is considered probable that the reaction is represented by the equations: $\text{O}:\text{OH} \cdot \text{H} + \text{MgRX} \rightarrow \text{H} \cdot \text{OHR} \cdot \text{OMgX} + \text{H}_2\text{O} \rightarrow \text{MgX} \cdot \text{OH} + \text{H}_2\text{O} + \text{R} \cdot \text{OH}$, these being analogous to the action of a magnesium alkyl haloid on formaldehyde: $\text{O}:\text{CH} \cdot \text{H} + \text{MgRX} \rightarrow \text{H} \cdot \text{CHR} \cdot \text{OMgX} + \text{H}_2\text{O} \rightarrow \text{MgX} \cdot \text{OH} + \text{R} \cdot \text{CH}_2 \cdot \text{OH}$.

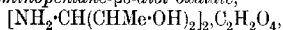
This reaction has been applied to the synthesis of ethyl, isobutyl, and isoamyl alcohols, good yields being obtained.
T. H. P.

Nitro- and Amino-glycols. II. ERICH SCHMIDT and RUDOLF WILKENDORF (*Ber.*, 1922, **55**, [B], 316—322; cf. A., 1919, i, 249).—The preparation of γ -nitro- and γ -amino-pentane- $\beta\delta$ -diols and a new preparation of β -nitrotrimethylene glycol are described.

β -Chloro- β -nitropropane- $\alpha\gamma$ -diol, m. p. 115—116° after previous softening, is obtained by passing a current of dry chlorine through a suspension of sodium β -nitrotrimethylene glycol in anhydrous ether; the corresponding dibenzoate has m. p. 114—115°. The chloronitro-glycol is converted by hydrogen in aqueous solution in the presence of pyridine and palladised barium sulphate into β -nitrotrimethylene glycol (Schmidt and Wilkendorf, *loc. cit.*).

An alcoholic solution of α -nitropropane- β -ol is converted by sodium dissolved in ethyl alcohol into α -nitro- α -sodiumpropane- β -ol, $\text{CH}_3\text{CH}(\text{OH})\text{CHNa} \cdot \text{NO}_2$, which is transformed by chlorine in the presence of anhydrous ether into α -chloro- α -nitropropane- β -ol, a colourless liquid, b. p. 91—92°/11 mm. The latter condenses with acetaldehyde in alkaline solution, giving γ -chloro- γ -nitropentane- $\beta\delta$ -diol, $\text{OH} \cdot \text{CHMe} \cdot \text{CCl}(\text{NO}_2) \cdot \text{CHMe} \cdot \text{OH}$, needles, m. p. 118—119°, b. p. 109—112°/0.2 mm. (corresponding dibenzoate, m. p. 115—116°), which is converted by hydrogen and palladised

barium sulphate in aqueous pyridine solution into γ -nitropentane- $\beta\delta$ -diol, m. p. 68—69° after previous softening, b. p. 109—110°/0.8 mm. The nitropentenediol is reduced by hydrogen in aqueous solution and in the presence of oxalic acid and palladised barium sulphate into γ -aminopentane- $\beta\delta$ -diol oxalate,



decomp. 178—179°.

H. W.

Chemical Composition and Physiological Characters of Brain Cephalin. FREDERIC FENGER (*J. Pharm. Expt. Ther.*, 1921, **18**, 51—62).—Cephalin is used as a haemostatic because it accelerates blood-clotting; this activity is retained practically unchanged for several years in ethereal solution; in the solid condition, moderately pure cephalin is more stable than the highly purified substance. Both the solubility of cephalin in water and its thromboplastic properties depend on the presence of sodium and potassium soaps of the fatty acids constituting the phosphatide.

G. B.

Chloropicrin as a Reagent for the Diagnosis of Mercaptans and Potential Mercaptans. SIR PRAFULLA CHANDRA RAY and RADHAKISHEN DAS (*T.*, 1921, **121**, 323—328).

The Practice of Precipitation with Lead. HEIDWIG LANG-ECKER (*Biochem. Z.*, 1921, **122**, 34—38).—Preparations of basic lead acetate were made by mixing lead acetate and litharge in various molecular proportions and treating the mixture with hot water. The maximum amount of litharge which can be taken up is three molecules. Schmidt's pentabasic lead acetate could not be realised. The solubility of the basic lead acetate falls off with increasing content of lead oxide.

H. K.

Preparation of Chlorinated Acetyl Chlorides. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 340872; from *Chem. Zentr.*, 1921, iv, 1101).—Chlorine substitution products of ethylene are treated with oxygen or gases containing oxygen in the presence of non-metals or their compounds as catalysts. Bromine or bromine compounds may be used. The oxidation of trichloroethylene, dichloroethylene, and perchloroethylene, which are themselves nonreactive with oxygen, is facilitated by the presence of small amounts of bromine, nitrogen, or sulphur compounds. Trichloroethylene is oxidised to dichloroacetyl chloride by oxygen in the presence of bromine, iodine, concentrated sulphuric acid, or concentrated nitric acid. Dichloroethylene may be similarly oxidised to chloroacetyl chloride. Perchloroethylene chloride is oxidised in the presence of bromine to trichloroacetyl chloride.

G. W. R.

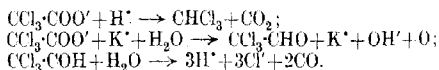
Esters of Ethylene Halohydrins. J. ALTWEGG and J. LAXDRIVON (U.S. Pat. 1393191).—Chloroethyl acetate is prepared by passing gaseous ethylene oxide into boiling acetyl chloride in equimolecular proportion, with immediate and quantitative yield of a product, b. p. 143—144°. Chloroethyl chloroacetate (b. p.

94–95°) is similarly prepared by the action of ethylene oxide on chloroacetyl chloride at 100°. Bromoethyl acetate is prepared by interaction for several hours of ethylene oxide with acetyl bromide at normal temperature and distillation. Chloroethyl benzoate is prepared by passing an equimolecular proportion of ethylene oxide slowly into benzoyl chloride at 190°, with further rise of temperature, followed by fractional distillation in a vacuum. Chloroethyl *p*-nitrobenzoate is obtained by treating *p*-nitrobenzoyl chloride with ethylene oxide and recrystallising from dilute alcohol.

CHEMICAL ABSTRACTS.

The Action of Ultra-violet Light on Aqueous Solutions of some Organic Acids and their Salts. F. M. JAEGER and G. BERGER (*Rec. trav. chim.*, 1922, **41**, 71–81).—It has been shown (Jaeger, A., 1912, i, 3) that the action of ultra-violet light on trichloroacetic acid to which ferric hydroxide has been added results in the formation of carbon dioxide and hexachloroethane. The authors have now established the fact that, in presence of excess of ferric hydroxide, a different reaction takes place, the products being carbon dioxide and chloroform. Further, if the acid is electrolysed in concentrated aqueous solution, its trichloromethyl ester is formed, together with carbonyl chloride and hydrochloric acid; this ester can be decomposed in presence of catalysts into carbon dioxide and hexachloroethane. A similar investigation of ferric tribromoacetate and pentachloropropionate has been carried out, the products obtained being carbon dioxide with bromoform and tetrachloroethylene respectively. In the case of potassium tribromoacetate, the solution gradually becomes acid under the influence of light, the reaction in dilute solution being represented by: $\text{CBr}_3\text{COO}' + \text{H}_2\text{O} + \text{K}' \rightarrow 2\text{H}' + \text{K}' + 3\text{Br}' + \text{CO} + \text{CO}_2$. In concentrated solution, a secondary reaction $\text{CBr}_3\text{COO}' + \text{H}' \rightarrow \text{CHBr}_3 + \text{CO}_2$ takes place simultaneously but a corresponding solution of the ferric salt yields hexabromoethane, the equation being $2\text{CBr}_3\text{COO}' + 2\text{Fe}''' \rightarrow \text{C}_2\text{Br}_6 + 2\text{Fe}'' + 2\text{CO}_2$, whilst the free acid is decomposed into bromoform and carbon dioxide.

Potassium trichloroacetate gives more complex results, probably due to the simultaneous occurrence of several different reactions. In fairly dilute solution, a small quantity of free carbon dioxide is formed, but in concentrated solution, carbon monoxide is obtained. For each molecule of the latter, two chlorine atoms are liberated and can be shown to exist in the ionic condition, but the ratio does not remain constant with prolonged exposure to light. Further, chloral is formed under certain conditions and possibly a little free oxygen also. The equations suggested are:



The corresponding decompositions of monochloroacetic and dichloroacetic acids have been studied by Benrath (A., 1911, ii, 681) and by Euler and Cassel (A., 1913, ii, 939); their results are compared

with the decomposition of potassium trichloroacetate, from which the authors obtained dichloroacetaldehyde: $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{COO}' + \text{K}' \rightarrow \text{CHCl}_2\cdot\text{COH} + \text{CO}_2 + \text{K}' + \text{Cl}'$. Three other substances have also been investigated: sodium chloromalonate, after two days, yields monochloroacetic acid which is partly transformed into glycollic and glyoxylic acids. The latter is probably formed directly from the monochloroacetic acid and not by oxidation of glycollic acid. Potassium α -bromophenylacetate yields bromine ions and benzaldehyde, the latter being obtained, according to the authors, together with formic acid, from the decomposition of mandelic acid, which is the primary product. Triphenylacetic acid, dissolved in a mixture of alcohol and water, yields carbon dioxide and a considerable quantity of triphenylmethane; with more concentrated solutions, the latter is partly replaced by triphenylcarbinol. The conclusion is drawn that the products of the photochemical decomposition of these ions in aqueous solution depend on the character of the other ions that may be present. The effect is seldom the same as that produced by heating the solution, and is scarcely comparable to the effects of electrolysis. The suggestion is made that the specific absorption of the solutions varies with the other ions that may be present and that this accounts for the different results obtained from the various salts of the same acid.

H. J. E.

The Acids of Montan Wax. HANS TROPSCH and A. KREUTZER (*Brennstoff Chem.*, 1922, **3**, 49).—The crude montanic acid, which has hitherto been regarded as the only acid present in montan wax and to which the formulae $\text{C}_{28}\text{H}_{56}\text{O}_2$ and $\text{C}_{26}\text{H}_{52}\text{O}_2$ have variously been ascribed, was esterified with methyl alcohol, and the resulting ester was separated into two fractions, boiling at $265\text{--}267.5^\circ/5$ mm. and $277.5\text{--}280^\circ/5$ mm., respectively. From each fraction the acid was again isolated and purified by fractional precipitation with magnesium acetate and recrystallisation from acetic acid. The acids obtained had equivalent weights 410.7 and 439.0, and m. p. 82° and $86\text{--}86.5^\circ$, respectively, and it is therefore concluded that the former is an acid of the formula $\text{C}_{27}\text{H}_{54}\text{O}_2$ for which the name *carboacerinic acid* is suggested, and the latter is pure montanic acid of the formula $\text{C}_{29}\text{H}_{58}\text{O}_2$.

G. F. M.

Erucic Acid and its Anhydride. D. HOLDE and C. WILKE (*Z. angew. Chem.*, 1922, **35**, 105).—Erucic acid, which has hitherto never been obtained free from arachic and other saturated fatty acids, was isolated in a pure condition by fractional precipitation of the partly purified acid with lithium acetate. The product obtained had an iodine value of 74.3 compared with 75.1 required by theory, and this figure affords the best criterion for the purity of the substance, as other constants, such as the melting point, are but little affected by the presence of moderate amounts of impurities. The anhydride was obtained, by heating the acid under pressure with acetic anhydride and purifying the product by recrystallisation from absolute alcohol. It has m. p. $46\text{--}46.5^\circ$,

is very resistant to *N*/10-aqueous alkali hydroxide and 25% hydrochloric acid, but is completely reconverted into erucic acid by boiling water. G. F. M.

The Action of Halogens on Ethyl Acetoacetate. L. I. SMITH (*J. Amer. Chem. Soc.*, 1922, **44**, 216—217).—When bromine is passed into ethyl acetoacetate by a rapid current of air which both introduces the bromine and sweeps out the hydrogen bromide as it is formed, the sole product is the α -bromo-ester. Thus under similar conditions the action of bromine on ethyl acetoacetate is similar to that of chlorine. W. G.

The C₄-Saccharinic Acids. II. The Preparation and Resolution of *dl*- α -Dihydroxybutyric Acid. Some Derivatives of the Optically Active Acids. J. W. E. GLATTFELD and FRANK V. SANDER (*J. Amer. Chem. Soc.*, 1921, **43**, 2675—2682; cf. A., 1921, i, 7).—*dl*- α -Dihydroxybutyric acid was prepared from β -hydroxypropionaldehyde by the addition of hydrogen cyanide and subsequent hydrolysis of the nitrile. It was resolved into its active components by means of brucine, and certain of the salts of the active acids were prepared. The configuration of the *l*- and *d*-acids are shown by oxidation to the corresponding malic acids to be respectively

$$\begin{array}{c} \text{OH H OH} & \text{OH H H} \\ | & | \\ \text{H} & \text{H} \\ \text{H C} & \text{— C — C} \end{array} \begin{array}{c} \text{CO}_2\text{H} \\ \text{H} \\ \text{CO}_2\text{H} \end{array}$$

The *d*-acid has $[\alpha]_D^{20} +14.97^\circ$; b. p. $96^\circ/3$ mm.; brucine salt, m. p. 169° ; $[\alpha]_D^{20} -20.79^\circ$; quinine salt, m. p. 149° ; $[\alpha]_D^{20} -106.4^\circ$; calcium salt, $[\alpha]_D^{20} +17.08^\circ$. The *l*-acid has $[\alpha]_D^{20} -14.86^\circ$; b. p. $96^\circ/3$ mm.; brucine salt, m. p. 169° ; $[\alpha]_D^{20} -32.67^\circ$; quinine salt, m. p. 149° ; $[\alpha]_D^{20} -122.9^\circ$; calcium salt, $[\alpha]_D^{20} -17.33^\circ$. W. G.

The Aldehyde Acids of the Succinic Series. E. CARRIÈRE (*Ann. Chim.*, 1922, **47**, 38—132).—In part, a more detailed account of work already published (cf. A., 1912, i, 410, 827; 1914, i, 806), with descriptions of new derivatives. Ethyl formylsuccinate gives a semicarbazone, m. p. 126° , a *p*-nitrophenylhydrazone, m. p. 100° , and a benzoyl derivative, m. p. $58-59^\circ$, b. p. $208-212^\circ/14$ mm. (cf. Wislicenus, Böklen, and Reuthe, A., 1909, i, 9). With aniline, it yields ethyl anilinoitaconate, m. p. 102° , which undergoes cyclisation in the presence of alcoholic potassium hydroxide, giving ethyl 1-phenylpyrroline-5-one-3-carboxylate, $\text{NPh} \begin{array}{c} \text{CH}_2\text{C} \\ \text{CO} \end{array} \begin{array}{c} \text{CO}_2\text{Et} \\ \text{CH}_2 \end{array}$.

Similarly, with *p*-toluidine, ethyl toluidinoitaconate, m. p. 113° , is obtained, and this on cyclisation yields ethyl 1-*p*-tolylpyrroline-5-one-3-carboxylate, m. p. $123-124^\circ$, which on saponification yields *p*-toluidine, sodium formate, and sodium succinate. With benzylamine, the products are ethyl benzylaminoitaconate, m. p. 54° , and ethyl 1-benzylaminopyrroline-5-one-3-carboxylate, m. p. 95° .

Ethyl formylsuccinate gives an oxime, which on distillation yields a mixture of ethyl- β -cyanopropionate, b. p. $114-115^\circ/18$ mm., and an oxime, m. p. 155° , of β -aldehydopropionic acid, isomeric with the one previously described (*loc. cit.*).

Ethylsuccinic acid when warmed with acetyl chloride gives an anhydride, b. p. $140^{\circ}/20$ mm., which gives a monoanilide, m. p. 118° , a dianilide, m. p. 205° , and an acid chloride, b. p. $94-95^{\circ}/14$ mm., of ethylsuccinic acid. The monoanilide when heated at 180° for one and a half hours yields the anil, $\text{CH}_2\text{CO} > \text{NPh}$, m. p. 74° .

Derivatives prepared from ethyl formylethylsuccinate are its semicarbazone, m. p. 113° ; its p-nitrophenylhydrazone, m. p. 113° ; its phenylurethane, b. p. $220^{\circ}/14$ mm. With phenylhydrazine, it yields ethyl 1-phenyl-5-ethylpyridazine-6-one-5-carboxylate, $\text{N} < \text{CH} \cdot \text{CH}(\text{CO}_2\text{Et}) > \text{CH}_2\text{CO} > \text{NPh}$, b. p. $225-240^{\circ}/15$ mm., which on saponification gives the free acid, m. p. 179° . With aniline, ethyl formylethylsuccinate yields ethyl anilinoethylitaconate, which on saponification gives 1-phenyl-4-ethylpyrroline-5-one-3-carboxylic acid, $\text{NPh} < \text{CH} \cdot \text{C}(\text{CO}_2\text{H}) > \text{CH}_2\text{CO} > \text{CH}_2\text{CO}_2\text{H}$, m. p. 190° , giving an ethyl ester, m. p. 99° . Similarly, ethyl p-toluidinoethylitaconate gives 1-p-tolyl-4-ethylpyrroline-5-one-3-carboxylic acid, m. p. 202° , giving an ethyl ester, m. p. 104° .

Thionyl chloride or phosphorus pentachloride reacts with β -aldehydopropionic acid to give chlorobutyrolactone, $\text{CH}_2 < \text{CH}_2 > \text{CHCl}$, b. p. $101^{\circ}/15$ mm., which with absolute alcohol gives the acetal, $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$.

With pyruvic acid and β -naphthylamine, the ester of β -aldehydopropionic acid gives ethyl naphthacinchoninylpropionate, m. p. 268° . With magnesium ethyl bromide, the aldehyde acid yields γ -ethyl- γ -octandiol, $\text{HO} \cdot \text{CET}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, m. p. 41° , b. p. $148^{\circ}/20$ mm., giving a monoacetate, b. p. $146-147^{\circ}/18$ mm. In the distillation of the diol, a small amount of material passes over at $80-90^{\circ}/20$ mm., and if this is boiled with 10% sulphuric acid the oxide, $\text{CH}_2 \cdot \text{CHET} > \text{O}$, b. p. $68-69^{\circ}/18$ mm., is obtained. The diol gives a diphenylurethane, m. p. 121° .

Ethyl β -aldehydopropionate condenses with ethyl malonate in the presence of diethylamine to give triethyl β -carboxymethylbutan-2,6-dicarboxylate, $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_2 \cdot \text{CO}_2\text{Et})_2$, b. p. $200^{\circ}/15$ mm., which on saponification yields the free acid, m. p. 122° . The acid, when heated on a water-bath with acetyl chloride, gives the anhydride, $\text{CO}_2\text{H} \cdot [\text{CH}_2]_2 \cdot \text{CH} < \text{CH}_2 \cdot \text{CO} > \text{O}$, m. p. 133° , from which a monoanilide, m. p. 151° , and a mono-p-toluidide, m. p. 207° , can be prepared. When β -aldehydopropionic acid, freshly prepared, is condensed with malonic acid in the presence of pyridine, adipenic acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH} \cdot \text{CO}_2\text{H})_2$, m. p. $208-210^{\circ}$, is obtained.

The acetal of β -aldehydopropionic acid (see above) reacts with magnesium ethyl bromide, giving 5-ethoxy-2:2-diethyltetrahydrofurfuran, $\text{CH}_2 \text{---} \text{CET}_2 > \text{O}$, b. p. $69^{\circ}/12$ mm., and γ -diethyloctan-

γ -diol, b. p. 154°/12 mm. (cf. Valeur, A., 1901, i, 317), from which the oxide, $\begin{matrix} \text{CH}_2\text{-C}(\text{C}_2\text{H}_5)_2 \\ | \\ \text{CH}_2\text{-C}(\text{C}_2\text{H}_5)_2 \end{matrix} > \text{O}$, b. p. 95—96°/14 mm., is obtained by the action of sulphuric acid. For the purpose of proving the identity of the previous diol, γ -ethylhexane- γ -diol, $\text{HO}\cdot\text{C}_2\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, b. p. 144—145°/20 mm., was prepared by the action of magnesium ethyl bromide on butyrolactone. It gives a *monoacetate*, and a *diphenylurethane*, m. p. 106°.

α -Ethyl- β -aldehydopropionic acid is prepared by hydrolysing ethyl formylethylsuccinate with oxalic acid in aqueous solution. The following derivatives are described: *semicarbazone*, m. p. 156°; *p*-nitrophenylhydrazone, m. p. 164°; *oxime*, m. p. 70°; α -ethyl- β -naphthacinchoninylpropionic acid, m. p. 260°; a *phenylhydrazide-phenylhydrazone*, $\text{NHPh}\cdot\text{N}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{Et})\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$, m. p. 175°; and an *ethyl ester*, b. p. 103—104°/20 mm., which gives a *semicarbazone* and a *p*-nitrophenylhydrazone. During the preparation of the ester, *ethoxybutyrolactone*, b. p. 114—115°/20 mm., is also obtained.

W. G.

The Rotatory Dispersive Power of Organic Compounds.

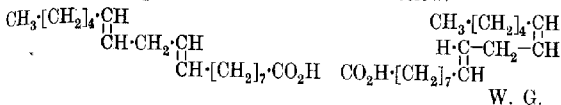
X. The Preparation and Properties of Pure Ethyl Tartrate.
THOMAS MARTIN LOWRY and JOHN OUTRAM CUTTER (T., 1922, **121**, 532—544).

Optical Activation of Racemic Acid by *l*-Malic Acid.

ALEX. MCKENZIE and NELLIE WALKER (T., 1922, **121**, 349—357).

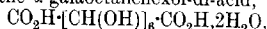
C₁₈-Acids. III. Four Tetrahydroxystearic Acids derived from Linoleic Acid, and their Significance with Regard to the Linoleic Acid of Common Oils. BEN H. NICOLET and HENRY L. COX (*J. Amer. Chem. Soc.*, 1922, **44**, 144—152; cf. A., 1921, i, 390; this vol., i, 106).—The linoleic acid used in this work was regenerated from the tetrabromide, m. p. 114°, itself prepared from the dried fatty acids of cotton-seed oil. The oxidation of the acid with cold alkaline permanganate yielded two sativic (tetrahydroxystearic) acids, namely, α -sativic acid, m. p. 153°, and β -sativic acid, m. p. 170° (cf. Rollet, A., 1909, i, 759, 760). When linoleic acid was treated with hypochlorous or hypobromous acid and the products were subsequently converted into sativic acids, two other isomerides were obtained. With hypochlorous acid, linoleic acid yielded *dichlorodihydroxystearic acid* as a viscous oil. Similarly, with hypobromous acid the product was *ditromodihydroxystearic acid*, an oil. Either of these compounds when heated with anhydrous potassium acetate and acetic anhydride gave *tetra-acetoxystearic acid*, which on hydrolysis with hot aqueous sodium hydroxide gave a mixture of γ -sativic acid, m. p. 144°, and δ -sativic acid, m. p. 135°. In the light of the above facts and the difference in behaviour between linoleic acid and oleic or elaidic acid on bromination and subsequent removal of the bromine by zinc, the authors are of the opinion that only two of the four possible stereoisomeric linoleic acids occur, at least in important

amounts, in linoleic acid as usually prepared. The most probable structures for this pair of isomerides are shown below.



Chemistry of the Sugars. III. H. KILLANI (*Ber.*, 1922, 55, [B], 493—505; cf. A., 1921, i, 304; this vol., i, 223).—The lengthening of the carbon chain of aldoses by the hydrocyanic method has hitherto been possible at only one end of the chain. The comparatively ready accessibility of *l*-mannohepturonic acid has now rendered it possible to lengthen the other end.

[With AUG. WINGLER].—The lactone of *l*-mannohepturonic acid is converted by hydrocyanic acid and ammonia in aqueous solution into the salt, $\text{NH}_4\cdot\text{CO}\cdot[\text{CH}(\text{OH})]_6\cdot\text{CO}_2\cdot\text{NH}_4$, microscopic leaflets, m. p. about 192° (decomp.) after darkening at about 180°, the yield being about 60% of that theoretically possible. The product is hydrolysed by boiling *N*/2-potassium hydroxide solution, thus giving the *potassium* salt, $\text{CO}_2\text{K}\cdot[\text{CH}(\text{OH})]_6\cdot\text{CO}_2\text{K}\cdot\text{H}_2\text{O}$, microscopic, lustrous leaflets, from which the following salts are obtained by double decomposition: *calcium* salt (+3.5H₂O), which is almost insoluble in water; *zinc* salt (+2H₂O), microscopic granules; *cadmium* salt (+5H₂O); *lead* salt, anhydrous granules; *normal quinine* salt (+3H₂O), small, lustrous needles, m. p. 201°; *normal brucine* salt (+9H₂O), m. p. (anhydrous) 170—171° (decomp.). The calcium salt is transformed by the calculated quantity of oxalic acid into the α -galaoctanehexol-di-acid,



well-defined, prismatic plates, decomp. 200° after darkening at about 190°. The corresponding *monolactone* is most readily prepared by decomposing the lead salt with hydrogen sulphide in the presence of water and evaporation of the filtrate at 60—70°; it crystallises in microscopic prisms without definite melting point.

The *dilactone*, short prisms, decomp. 200°, which dissolve sparingly in water, is obtained by dissolving the calcium salt in warm dilute hydrochloric acid and concentrating the solution at 55°; it does not reduce Fehling's solution. From its mode of production, two configurations are possible for the dibasic acid for which, by reason of its optical inactivity, the annexed symmetrical formula is adopted. Drastic reduction of the dicarboxylic acid by means of hydriodic acid should lead to the formation of sebacic acid, which, up to the present, has not been thus isolated, an amorphous, apparently unsaturated, acid being obtained in its place.

The dilactone gives a *diphenylhydrazide*, $\text{C}_{30}\text{H}_{26}\text{O}_8\text{N}_4$, colourless, microscopic leaflets, m. p. 285—286°, after becoming discoloured at 250°.

[With AUG. WINGLER].—The following derivatives of *l*-manno-

*m*⁴

hepturonic acid have been prepared: *phenylhydrazone-phenylhydrazide*, $C_{19}H_{24}O_6N_4$, colourless, microscopic leaflets, m. p. 199° (from the lactone of *l*-mannohepturonic acid and four molecular proportions of phenylhydrazine in aqueous acetic acid solution at the atmospheric temperature); *phenylosazone-phenylhydrazide*, $C_{25}H_{28}O_5N_6$, yellow needles, m. p. $203-204^\circ$ (from the same mixture as used for the preceding compound, but in boiling solution); *p*-nitrophenylhydrazone, long, intensely yellow, coarse needles, m. p. 167° (decomp.) when rapidly heated; *semicarbazone*, microscopic crystals, m. p. $174-175^\circ$ (decomp.).

l-Mannohepturonic acid behaves as an aldose towards iodine and sodium hydroxide solution; it is interesting to note that ketonic sugars which contain a terminal methyl group adjacent to $CH(OH)$ or CO appear to react similarly (cf. the production of iodoform from lactic or lævulinic acid).

Polyhydroxy-acids are converted into their lactones with very varying degrees of readiness; many examples are quoted and discussed, but it does not seem possible at present to give a satisfactory explanation of the observed facts.

β -Galaheptonic acid is oxidised by nitric acid to the monolactone of *\beta*-galaheptanepentoldi-acid, well-defined crystals which darken between 145° and 180° without actually melting. It could not be converted into a di-lactone. The salts of the corresponding dibasic acid appear to have little tendency towards crystallisation.

It is considered that Bergmann's recently proposed definition of a sugar (this vol., i, 227) lays too great emphasis on osazone formation, and it is pointed out that, according to it, ordinary sucrose would no longer be regarded as a sugar.

H. W.

Mutarotation of Dextrose under the Influence of Sodium Chloride. HANS MURSCHHAUSER (*Biochem. Z.*, 1921, 125, 158-178).—Addition of pure sodium chloride to dextrose solution undergoing mutarotation causes an increase of the velocity of mutarotation inversely proportional to the increase of concentration of the salt. Impurities in sodium chloride influence the velocity constant considerably. Ordinary cooking salt almost doubles the constant, whilst a fused, analytically pure sodium chloride showed an eight-fold increase due to development of alkali.

H. K.

The Influence of Sodium Chloride on the Mutarotation of Dextrose in Hydrochloric Acid Solution. I. HANS MURSCHHAUSER (*Biochem. Z.*, 1921, 126, 40-54).—In decinormal hydrochloric acid solution, the velocity constants for the mutarotation of dextrose show an increase proportional to the concentration of sodium chloride in the solution.

H. K.

The Influence of Dextrose on the Dialysis of Sucrose through a Parchment Membrane. The Possibility of the Separation of Dextrose from Sucrose by Dialysis. LEON A. CONGDON and HARRY R. INGERSOLL (*J. Amer. Chem. Soc.*, 1921, 43, 2588-2597).—In mixtures of dextrose and sucrose, the

influence of dextrose on the dialysis of sucrose is of such a character as to keep the ratio of the percentage of original dextrose to percentage of original sucrose dialysed approximately constant at about 2.5:1, irrespective of the concentration of the sucrose, provided that the concentration of the dextrose is not less than 2% and the time of dialysis has exceeded three hours. In solutions containing less than 2% of dextrose, the dextrose dialyses at a much greater rate and at a dextrose concentration of 0.125% the above ratio becomes 5:1. With such a dilute solution of dextrose containing 6.25% of sucrose it was found that the whole of the dextrose was removed after fifty-one hours' dialysis. W. G.

An Improved Method for Preparing Raffinose. E. P. CLARK (*J. Amer. Chem. Soc.*, 1922, **44**, 210—213; cf. Hudson and Harding, A., 1914, i, 1166).—In this improved method the cotton-seed meal is extracted by percolation, which must be done quickly. The extract is purified by treatment with basic lead acetate and the excess of lead is removed by the addition of oxalic acid. The sugar is then thrown out of solution as the insoluble calcium raffinosate. To regenerate the raffinose, this compound is decomposed with carbon dioxide as in the manufacture of sucrose. The resulting solution is evaporated under diminished pressure until it contains 70—75% of total solids and then the raffinose is caused to crystallise out by the addition of alcohol. A simple stirring device for the rapid and convenient carbonation of the raffinosate is described. W. G.

Xylan. E. SALKOWSKI (*Z. physiol. Chem.*, 1921, **117**, 48—60).—Improvements in the author's method of preparation of xylan (A., 1902, i, 293) are described. The formula, $C_{10}H_{18}O_9$, previously given to xylan, is replaced by $C_5H_8O_4$. On hydrolysis, xylan takes up one molecule of water and is converted into xylose. A factor is introduced for calculating xylose from the cuprous oxide obtained on heating with Fehling's solution. S. S. Z.

Sulphur in Agar. CARL NEUBERG and HEINZ OHLE (*Biochem. Z.*, 1921, **125**, 311—313).—Preliminary observations pointing to the existence of sulphur in organic combination in agar. Hydrogen sulphide is evolved by bacterial action and hydrolysis sets free sulphuric acid. H. K.

The Change of Glycogen under the Influence of Light. GUSTAV BAYER (*Biochem. Z.*, 1921, **124**, 97—99).—Glycogen exposed to sunlight becomes insoluble in water. From its reactions the author considers this to be due either to a polymerisation or to a physical alteration of the surface of the glycogen whereby the hydrophilic sol-forming surface layers are transformed into a dehydrated form which can no longer show imbibition. H. K.

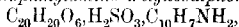
Cellulose Acetate from Wood Cellulose. ERIK HAGGLUND, NILS LÖFMANN, and EDUARD FÄRBER (*Cellulosechemie*, 1922, **3**, 13—19).—Cellulose extracted from sawdust by the action of 40% hydrochloric acid is not a suitable material for the preparation of

cellulose acetate. With sulphite wood pulp, satisfactory products can be obtained after a suitable preliminary treatment. Dehydration of the cellulose by heating with acetic acid and acetic anhydride is unfavourable to the acetylation process; traces of water are favourable. The best products were obtained by the following procedure: 5 grams of sulphite cellulose are subjected to a preliminary treatment with 20 grams of acetic acid (100%), 0.5 gram of water, and 0.5 gram of sodium hydrogen sulphate at 50–70° for seventeen hours; 25 grams of acetic anhydride are added to the cooled mixture, the temperature not being allowed to rise above 60°. When the cellulose has dissolved, the reaction is completed by warming at 70° for about half an hour; 5.5–6 c.c. of water are then added and the viscous solution is digested at 50° for sixty-five to seventy hours in order to obtain a cellulose acetate which is soluble in acetone and insoluble in chloroform. J. F. B.

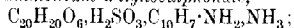
The Solubility of Cellulose Acetate in the Salts of the Alkali- and Alkaline-earth Metals. K. SCHWEIGER (*Z. physiol. Chem.*, 1921, 117, 61–66).—The solubility of various preparations of cellulose acetate in concentrated solutions of a number of the above salts is given. With concentrated salt solutions, there is no scission of the acetyl groups, but the cellulose molecule is degraded.

S. S. Z.

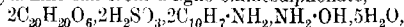
Constitution of Pine Lignin. II. PETER KLASON (*Ber.*, 1922, 55, [B], 448–455).—It has been shown previously that α -lignin, $C_{22}H_{22}O_7$, is the main constituent of pine wood. Since it contains an acetyl group which is eliminated as acetic acid during the sulphite treatment, the residue, $C_{20}H_{20}O_6$, must be present in α -lignosulphonic acid. The homogeneity of calcium α -lignosulphonate is established by the uniformity of the specimens of the β -naphthylamine salt obtained from it by fractional precipitation with β -naphthylamine hydrochloride. In course of time the sulphite liquors deposit gypsum and darken in colour and then give a β -naphthylamine salt containing a less sulphur content than is normal, thus confirming the author's view that the presence of calcium inhibits the formation of free lignosulphonic acid during the boiling process and that the occurrence of the latter is the cause of the so-called "black boiling." The following salts have been prepared: α -naphthylamine α -lignosulphonate,



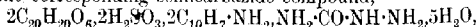
a yellowish-white precipitate which, in contrast to the β -naphthylamine derivative, is not a cyclic compound; β -naphthylamine α -methylignosulphonate, $C_{31}H_{31}O_6NS$, an internal salt; β -naphthylamine salt from ammonium α -lignosulphonate,



β -naphthylamine salt from α -ligno-oximesulphonate,

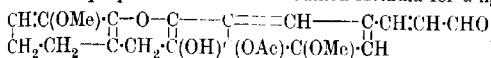


and the corresponding semicarbazide compound,



the composition of which indicates that the acid, at any rate in its salt, has double the molecular weight ascribed to it previously.

α -Lignosulphonic acid is oxidised by hydrogen peroxide at the atmospheric temperature, and the product is precipitated as the α -naphthylamine salt, $C_{40}H_{38}O_{11}N_2S$, the composition of which indicates that the aldehydic has become oxidised to the carboxyl group and a methylene to the ketonic group. β -Naphthylamine α -lignosulphonate can be acetylated by means of acetic anhydride, two acetyl groups being introduced thereby into the molecule, thus proving the presence of two hydroxyl groups one of which can be methylated, and is therefore united to the benzenoid nucleus, whereas the other is more positive in character and is hence attached to a more aliphatic group. These observations, coupled with the behaviour of α -lignosulphonic acid towards hydrogen peroxide, lead the author to propose the annexed modified formula for α -lignin :



H. W.

Lignin. I and II. KARI. H. A. MELANDER (*Cellulosechemie*, 1921, 2, 41—43, 69—73; cf. A., 1921, i, 849).—Among the products obtained by the addition of sodium chloride to waste sulphite liquors is the sodium salt of an α -ligninsulphonic acid. One hundred grams of the crude product, containing about 27% of sodium chloride, yield about 25 grams of the free acid; the sodium salt contains 2.96—3.78% Na and 4.41—5.10% S. The acid is precipitated by aromatic bases, the *o*-toluidine salt being particularly examined. Analysis gave results which indicated formulæ varying from $C_{31}H_{34}O_{10}$ to $C_{34}H_{44}O_{11}$ for lignin; the latter substance was shown to contain an acetyl group. The products analysed were, however, admittedly mixtures.

CHEMICAL ABSTRACTS.

Methylation of Lignin. E. HEUSER, R. SCHMITT, and L. GUNDEL (*Cellulosechemie*, 1921, 2, 81—86).—Lignin obtained by the action of hydrochloric acid (*d* 1.2) on sawdust, when treated with methyl sulphate and sodium hydroxide, gave 96% of *methyl-lignin* (methoxyl content, 20.65%, increasing by repeated methylation to 26.29%). The methoxyl content is completely removed only by repeated treatment with hydrochloric acid in a sealed tube, when a product is obtained containing 67.45—69.30% C and 4.16—4.50% H. Methyl-lignin prepared from this substance contained only 5.79% of methoxyl. A sodium hydroxide solution of lignin, prepared at 170° in an autoclave, when methylated with methyl sulphate had a methoxyl content of 24.7%.

CHEMICAL ABSTRACTS.

Derivatives of Straw Lignin. F. PASCHKE (*Cellulosechemie*, 1922, 3, 19—21; cf. A., 1921, i, 772).—Derivatives have been prepared from lignin obtained by the digestion of straw with sodium carbonate and having a composition corresponding with $C_{40}H_{45}O_{13}$. With phenylhydrazine, on heating, a violent reaction takes place and formation of aniline, water, and ammonia. The yield of ligninphenylhydrazone, $C_{58}H_{57}N_6O_{10}$, is 80%; it is soluble in alcohol, acetone, and tetrachloroethane, the solutions drying in

the form of a brown varnish film. With nitrosodimethylaniline (1 part), lignin (1.5 parts), concentrated hydrochloric acid (1 part), and acetic acid (50 parts), on boiling for two hours, a condensation product is obtained having the properties of a dyestuff, *lignoeyanin*, $C_{104}H_{101}N_{16}O_{26}$, analogous to galloeyanin and dyeing silk directly from dilute acetic acid solutions, cotton only when mordanted; the colour is brownish-violet. By the prolonged action of sulphuryl chloride at the ordinary temperature, a product containing 12.22% of chlorine and 11.04% of sulphur is obtained; with sulphuryl chloride at 100° under pressure, the resulting product contains 38.22% of chlorine and no sulphur; both products are free from methoxyl groups; the solutions of the latter dry as a varnish. With phosphorus pentachloride dissolved in excess of tetrachloroethane, lignin reacts violently with formation of a compound containing 19.18% of chlorine, corresponding with the formula $C_{38}H_{16}O_{15}Cl_5$. This compound also gives solutions which dry to a varnish.

J. F. B.

Synthesis of the Humic Acids. WILHELM ELLER (*Brennstoff Chem.*, 1922, 3, 49—52 and 55—56; cf. A., 1920, 1, 733).—Polemical. The author maintains that the humic acids contain a benzene nucleus, are closely related to the substances prepared by him by the oxidation of phenols in alkaline solution, and are not derivatives of furan as suggested by Marcusson (A., 1921, i, 313; ii, 590) and by Jonas.

G. F. M.

Natural and Artificial Humic Acids. K. G. JONAS (*Brennstoff Chem.*, 1922, 3, 52—55).—Polemical. The author contends that Eller's synthetic products do not resemble the naturally occurring humic acids.

G. F. M.

Complex Metallic Ammines. VII. Conductivities of Diethylenediaminecobaltic Bromides. JAMES COOPER DUFF (T., 1922, 121, 450—454).

Constitution of Glutamine. H. THIERFELDER (*Z. physiol. Chem.*, 1921, 114, 192—198; cf. Johnson and Guest, A., 1912, i, 316).—1-Acetyl-2-thiohydantoin-5-propionamide prepared from *d*-glutamine and potassium thiocyanate has m. p. 209° and on hydrolysis yields 2-thiohydantoin-5-propionic acid. The latter compound on treatment with chloroacetic acid was converted into hydantoin-5-propionic acid. Owing to this reaction, which is characteristic of the α -amino-acids, the author ascribes the following formula to glutamine: $NH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$.

S. S. Z.

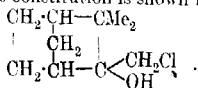
Cystine. ALICE R. THOMPSON MERRILL (*J. Amer. Chem. Soc.*, 1921, 43, 2688—2696).—In the preparation of cystine from wool by hydrolysis with hydrochloric acid, the yield is materially increased by boiling for twelve hours instead of three. The zone of hydrogen-ion concentration most favourable for the precipitation of the cystine from the resulting solution is 10^{-3} to 10^{-4} , and in order to obtain the cystine free from tyrosine it is advisable to precipitate it from a solution having a concentration of about 10^{-3} .

Using sodium acetate as a buffer in the hydrolysed wool solution, it was found that when the maximum yield of cystine was obtained the hydrogen-ion concentration was 10^{-4} . The highest yield of cystine thus obtained was 5.2% of the weight of the wool taken. For the purification of crude cystine, its solution may be decolorised by norit which has been previously boiled with dilute hydrochloric acid, and in that case very little of the cystine is absorbed. W. G.

Synthesis of 2-Hexosamic Acids and 2-Hexosamines. P. A. LEVENE (*Biochem. Z.*, 1921, **124**, 37—83).—A detailed summary of work previously published by the author and his co-workers on this subject (A., 1915, i, 601, 782, 944; 1916, i, 203, 712, 713; ii, 3; 1917, i, 633; 1918, i, 530, 532; 1919, i, 475, 476; 1921, i, 318). H. K.

Monochlorocarbamide. Preparation of Chlorohydrins by its Action on Ethylenic Hydrocarbons. ANDRÉ DETOUFF (*Bull. Soc. chim.*, 1922, [iv], **31**, 169—176; 176—181; cf. this vol., i, 236).—The results obtained by using the method previously described (*loc. cit.*) with different ethylenic hydrocarbons are detailed. With amylene, the product is the chlorohydrin of amylene glycol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CHMeCl}$, which, when heated at 130° with anhydrous oxalic acid, gives chloroamylene and with alcoholic potassium hydroxide yields amylene oxide. When warmed with aniline, the chlorohydrin gives methyl isopropyl ketone. β -Dimethylbutylene gives with chlorocarbamide β -chloro- γ -hydroxy- β - γ -dimethylbutane. Δ^8 -Hexene yields β -chloro- γ -hydroxyhexane. ϵ -Methyl- Δ^2 -hexene yields α -chloro- β -hydroxy- ϵ -methylhexane, b. p. 97 — $98^\circ/23$ mm.; d_4^{20} 1.044; n_D^{20} 1.45662. On oxidation with chromic acid, it gives α -chloro- ϵ -methylhexan- β -one, b. p. $118^\circ/40$ mm. Δ^8 -Octene yields β -chloro- γ -hydroxyoctane, b. p. 99 — $110^\circ/14$ mm.; d_4^{20} 1.001; n_D^{20} 1.45232. On oxidation, it yields α -chloroethyl pentyl ketone, b. p. $92^\circ/16$ mm., giving a semicarbazone, m. p. 145° . With alcoholic sodium hydroxide, this chlorohydrin gives β -octene oxide, $\text{CH}_3(\text{CH}_2)_4\text{CH}\cdot\text{CH}(\text{OH})\text{Me}$, b. p. 70 — $75^\circ/18$ mm.; d_4^{18} 0.858; n_D^{18} 1.42085.

With cyclic hydrocarbons, the following results were obtained. Styrene yielded α -chloro- β -hydroxy- β -phenylethane, b. p. $128^\circ/17$ mm.; d_4^{20} 1.225; n_D^{20} 1.55405, which with sodium ethoxide gave ethyl β -hydroxy- β -phenylethyl ether, b. p. 240 — $245^\circ/760$ mm.; d_4^{20} 1.054. Cyclohexene yielded 1-chloro-2-hydroxycyclohexane, b. p. 84 — $85^\circ/16$ mm.; m. p. 8° ; d_4^{20} 1.138; n_D^{20} 1.49097, which with potassium hydroxide in anhydrous ether gave cyclohexyl oxide. Under similar conditions, menthene gave the chlorohydrin of menthene glycol, b. p. 120 — $125^\circ/14$ mm.; d_4^{20} 1.063; n_D^{20} 1.48422. Camphene gave the chlorohydrin of camphene glycol, m. p. 96° ; b. p. 125 — $130^\circ/14$ mm. Its constitution is shown by its behaviour to be



W. G.

Guanidonium Salts. W. MARCKWALD and F. STRUWE (*Ber.*, 1922, **55**, [B], 457—463).—Guanidonium chlorate and perchlorate have been described by Marckwald (D.R.-P. 309297, 309298) as powerful explosives (cf. Mannelli and Bernardini, *Brit. Pat.* 155627). The latter is obtained readily by heating a mixture of equivalent amounts of dicyanodiamide and ammonium perchlorate at 160° , and thus forms a convenient initial material for the preparation of guanidine, the following salts of which are now described. *Guanidonium thiosulphate* (from an alcoholic solution of guanidonium perchlorate and saturated aqueous potassium thiosulphate), $(\text{CN}_3\text{H}_6)_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$; *guanidonium sulphite*, $(\text{CN}_3\text{H}_6)_2\text{SO}_3$, a colourless, crystalline compound; *guanidonium hydrogen sulphide*, $(\text{CN}_3\text{H}_6)\text{HS} \cdot \text{H}_2\text{O}$, yellow leaflets; *guanidonium xanthate*, $\text{CN}_3\text{H}_6 \cdot \text{S} \cdot \text{CS} \cdot \text{OEt}$, pale yellow crystals, m. p. 113° ; *guanidonium borate*, $(\text{CN}_3\text{H}_6)_2\text{B}_3\text{O}_7 \cdot 5\text{H}_2\text{O}$, colourless crystals; *guanidonium stannate*, $(\text{CN}_3\text{H}_6)_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$, long, lustrous crystals; *guanidonium metasilicate*, $(\text{CN}_3\text{H}_6)_2\text{SiO}_3 \cdot x\text{H}_2\text{O}$; *guanidonium formate*, m. p. $70-75^\circ$; *guanidine nitromethane*, $\text{CN}_3\text{H}_3 \cdot \text{CH}_2 \cdot \text{NO}_2$, small, colourless needles; *guanidonium phenoxide*, $\text{CN}_3\text{H}_6 \cdot \text{OPh}$, colourless crystals, m. p. 67° ; *guanidonium p-tolylxide*, m. p. $147-150^\circ$; *guanidine benzenesulphonamide*, $\text{CN}_3\text{H}_5 \cdot \text{NH}_2 \cdot \text{SO}_3\text{Ph}$, m. p. 183° (decomp.); *guanidine phthalimide*, $\text{CN}_3\text{H}_5 \cdot \text{NH} : (\text{CO})_2 \cdot \text{C}_6\text{H}_4$, m. p. $176-179^\circ$ (decomp.).

Guanidine has been obtained in the solid state by mixing alcoholic solutions of guanidonium perchlorate and potassium hydroxide, removal of precipitated potassium perchlorate and concentration of the solution in a vacuum at $30-35^\circ$; the product contains 92.73—99.55% of guanidine and melts somewhat indefinitely at about 50° . It has been described by Veley (*T.*, 1908, **93**, 652) as a weak base, but his observations are not in harmony with those of Ostwald or of Morrell and Bellars (*T.*, 1907, **91**, 1012). It is now found that solutions of guanidonium hydroxide behave like those of the alkali hydroxides towards solutions of metallic salts: the strength of the base is established in addition by its ability to form stable salts with very weak acids. H. W.

Pyrofulmin, a Decomposition Product of Mercury Fulminate. LANGHANS (*Z. ges. Schiess. u. Sprengstoffw.*, 1922, **17**, 9—11, 18—21, 26—28).—Mercury fulminate is completely changed into a non-explosive substance by heating at 90° for about one hundred hours. The product is yellowish-brown and shows the unchanged crystalline form of mercury fulminate. The change can be followed by determining the mercury in the substance electrolytically. A gradual rise takes place from 70.42% (the value for the pure fulminate) to between 74 and 76.6% in the non-explosive substance, which is named *pyrofulmin*. *Pyrofulmin* is insoluble in water and in the usual organic solvents, and is neutral to litmus. It swells up on heating, giving off white, choking vapours. Its content of mercury is not constant, but never exceeds 76.6%, nitrogen 9.88%, carbon 6.21%, oxygen 7.51%. The loss of weight of the fulminate on heating therefore consists mainly of

carbon and oxygen. Pyrofulmin is probably not a definite compound. Its reactions point to its being a mixture of mercuric oxycyanide, $\text{Hg}(\text{OCN})\cdot\text{CN}$, with a little mercuric oxide.

H. C. R.

Solubility of Potassium Ferrocyanide in Water. Ice Curve and Cryohydric Point. E. FABRIS (*Gazzetta*, 1921, **51**, ii, 374—380).—The solubility of potassium ferrocyanide in grams of the salt per 100 grams of water between 0° and 100° is represented by two almost rectilinear curves meeting at 80° . This temperature is given in Landolt's tables as the transformation point of the hydrate, $\text{K}_4\text{Fe}(\text{CN})_6\cdot 3\text{H}_2\text{O}$ into $\text{K}_4\text{Fe}(\text{CN})_6\cdot x\text{H}_2\text{O}$, but evidence of this transformation is obtainable neither by the dilatometric method nor by analysis of the solid phase. The author has traced the freezing-point curve, the cryohydric point being -1.58° , which corresponds with the concentration 13.1 grams of the anhydrous salt per 100 grams of water.

T. H. P.

Symmetrical Diisopropylhydrazine and its Derivatives.

HARRY L. LOCHTE, JAMES R. BAILEY, and WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1921, **43**, 2597—2603).—Dimethylketazine may readily be reduced by means of colloidal platinum, using Skita's method (cf. A., 1913, i, 53, 54), and a yield of more than 90% of *s*-diisopropylhydrazine is obtained provided there is enough hydrochloric acid present to neutralise the base formed. *s*-Diisopropylhydrazine, $\text{CHMe}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CHMe}_2$, is a pale straw-coloured liquid, b. p. $124\text{--}124.5^\circ/740\text{ mm.}$; n_D^{20} 1.4087; d_4^{20} 0.7712, giving a hydrochloride, m. p. 198° (corr.), an oxalate, and crystalline condensation products with potassium cyanate and phenylcarbimide. With phenylthiocarbimide, it yields diisopropylphenylthiosemicarbazide, $\text{CHMe}_2\cdot\text{NH}\cdot\text{N}(\text{CS}\cdot\text{NHPh})\cdot\text{CHMe}_2$, m. p. 129.5° (corr.).

W. G.

The Preparation of Mercury Dialkyl Compounds from the Grignard Reagent.

C. S. MARVEL and V. L. GOULD (*J. Amer. Chem. Soc.*, 1922, **44**, 153—157).—The reaction between an excess of the Grignard reagent and a mercuric haloid furnishes a very satisfactory method for the preparation of mercury dialkyl compounds, provided the proper precautions are observed. Any unchanged magnesium must be removed from the Grignard reagent before adding the mercuric haloid, and after the whole of the mercuric haloid has been added, the mixture must be boiled for ten to twelve hours to complete the reaction. The following compounds have been prepared by this method: mercury dimethyl, b. p. $92^\circ/740\text{ mm.}$ (corr.); mercury diethyl, b. p. $97\text{--}99^\circ/125\text{ mm.}$; mercury dipropyl, b. p. $81\text{--}84^\circ/19\text{ mm.}$; mercury diisopropyl, b. p. $119\text{--}121^\circ/125\text{ mm.}$; mercury dibutyl, b. p. $120\text{--}123^\circ/23\text{ mm.}$ When a magnesium alkyl bromide reacts with an excess of mercuric chloride, a mixture of mercury alkyl chloride and bromide is obtained. To obtain each of these compounds pure, the halogen of the alkyl haloid must be the same as that of the mercuric salt.

W. G.

Mixed Organometallic Compound of Aluminium. V. THOMAS (*Compt. rend.*, 1922, 174, 464—465).—Aluminium when left in contact for a long time with methylene iodide in the absence of a solvent reacts with it without any appreciable evolution of gas, the mixture ultimately setting solid. A white, crystalline compound was obtained which it was not possible to purify, as it was highly reactive. If the aluminium and methylene iodide are allowed to react in the presence of anhydrous ether, a gas is evolved which is absorbed by bromine and attacked by permanganate. The gas has the formula $(\text{CH}_2)_n$, but apparently is not ethylene. The solid product of the reaction in ether is also highly reactive.

There is some indication that other metals, and in particular lead, are also capable of attacking methylene iodide in the absence of a solvent without any gas being evolved.

W. G.

Kinetics of Open Saturated Chains of Carbon Atoms in Relationship to the Baeyer Strain Theory. Z. WOJNICZ-SIANOZENCKI (*Roczniki Chemji*, 1921, 1, 244—275).—It is shown that the kinetics of an open saturated chain of carbon atoms may be treated by the theory of probabilities. If it be admitted that the limiting distance over which the carbon atom can exert a chemical force is not more than 2.101 times that which is normal for the two atoms connected by a single linking, then it is shown that the probability of the formation of polymethylene rings containing various numbers of carbon atoms follows the order $\xi_2 > \xi_5 > \xi_6 > \xi_7 > \xi_3 > \xi_4 > \xi_8$, where ξ_n is the probability of formation of an n -membered carbon ring. This indicates that the double linking is more easily formed than the five-membered ring, and this more easily than the six-membered ring, and so on. This appears to be in keeping with experimental work, which is often contradictory to the usually adopted hypothesis.

J. F. S.

[**Lignite Producer Tar.**] FRANZ FISCHER (*Ber.*, 1922, 55, [B], 505—506).—A criticism of Ruhemann's recent communication (this vol., i, 22).

H. W.

The Ethylation of Benzene and Naphthalene. C. H. MILLIGAN and E. EMMET REID (*J. Amer. Chem. Soc.*, 1922, 44, 206—210).—Balsohn's method (cf. A., 1879, 785) for the ethylation of benzene may be modified by the introduction of high speed stirring so that ethylene can be made to react with benzene in the presence of aluminium chloride at 70—90° so rapidly and completely that this becomes a practical method for the ethylation of benzene. A mixture of ethyl-, diethyl-, etc., up to hexaethyl-benzenes is obtained, but may fairly readily be separated into its components. If the polyethylbenzenes are stirred with benzene in the presence of the aluminium chloride from the previous reaction, they will give up some of their ethyl groups to the benzene. In a similar way, naphthalene may readily be ethylated by stirring it vigorously in benzene with polyethylbenzenes and aluminium chloride at 80°.

W. G.

The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. V. Heteronuclear Dinitro-derivatives. HAROLD BURTON and JAMES KENNER (*T.*, 1922, 121, 489—496).

The Nitration of *m*-Nitrotoluene. OSCAR LISLE BRADY (*T.*, 1922, 121, 328—331).

Some New Derivatives of Sulphobenzide [Diphenylsulphone]. ETG. GRANDMOUGIN (*Compt. rend.*, 1922, 174, 393—395).—In part a recapitulation of previous work (this vol., i, 251). 3:3'-Diaminosulphobenzide can be converted into the corresponding halogenated derivatives by the Sandmeyer reaction. 3:3'-Dichlorosulphobenzide has m. p. 108°; 3:3'-di-iodosulphobenzide has m. p. 158°. 2:2'-Dinitrosulphobenzide, m. p. 189°, was obtained by the oxidation of *o*-dinitrophenyl sulphide with potassium dichromate and sulphuric acid. To obtain unsymmetrical derivatives of sulphobenzide, sulphinic acids may be condensed with chloronitro-derivatives of aromatic hydrocarbons. Thus 1-chloro-2:4-dinitrobenzene and β -naphthalenesulphinic acid yield 2:4-dinitrophenyl- β -naphthylsulphone, m. p. 228°. W. G.

Theory of Carbonium Compounds. F. KEHRMANN (*Ber.*, 1922, 55, [B], 507—511).—A reply to Hantzsch (this vol., i, 24, 25).—The author is not convinced of the superiority of Hantzsch's complex formulæ over his own quinolide formulæ, or of the incorrectness of his theory of the sexavalency of carbon in carbonium salts (*A.*, 1918, i, 311). H. W.

Elimination of Hydrogen from Aromatic Nuclei and Union of the Latter by means of Aluminium Chloride. V. Experiments with Benzil, Stilbene, and Phenanthrene. R. SCHOLL and G. SCHWARZER (*Ber.*, 1922, 55, [B], 324—330; cf. Scholl and Seer, this vol., i, 258).—Phenanthraquinone is formed in 25% yield when an intimate mixture of benzil and anhydrous aluminium chloride is heated at 120° during one hour; in addition, two substances are produced which are soluble in sodium hydroxide solution; these have not been examined fully.

Stilbene is readily converted by aluminium chloride into a polymeride which softens at about 165° after previous darkening and becomes carbonised at a higher temperature; according to determinations of molecular weight in boiling benzene, polymerisation has not proceeded beyond the trimeric stage (cf. Liebermann and Mitter, *A.*, 1912, i, 464). The substance is oxidised by potassium permanganate or chromic acid in the presence of glacial acetic acid without giving well-characterised products; it is converted by nitric acid (*d* 1.15) at 150° into a nitrogen-free mixture of acids ($C_8H_5O_3$)₂.

Phenanthrene is converted by aluminium chloride in the presence of nitrobenzene at the atmospheric temperature into a black mass. In the presence of carbon disulphide, on the other hand, a yellow, amorphous product, decomp. about 225°, is obtained which is not identical with the substance derived from stilbene. Its nature

has not been elucidated fully, but it is possibly a polymeric of phenanthrene, although analyses of it agree better with the composition ($C_{14}H_{11}$)₂; it is readily converted by nitric acid into an amorphous nitro-compound. H. W.

New Preparation of cycloAlkylamines. ALPHONSE MAILHE (*Compt. rend.*, 1922, **174**, 465—467).—*cyclo*Hexanone gives with hydrazine hydrate a mixture of its hydrazone, b. p. 195°, and its ketazine, b. p. 270°. When the mixed vapours of these two substances are passed along with hydrogen over nickel at 180° an excellent yield of *cyclo*hexylamine together with some *dicyclo*hexylamine is obtained. Under similar conditions, *o*-methyl*cyclo*hexanone gives its hydrazone and its ketazine, and these when hydrogenated together give principally *o*-methyl*cyclo*hexylamine, b. p. 150°; d_4^{20} 0.8836; giving a *hydrochloride*, m. p. 280°. A small amount of *di*-*o*-methyl*cyclo*hexylamine, b. p. 268—270°, giving a *hydrochloride*, m. p. 226°, is also obtained. *m*-Methyl*cyclo*hexanone only gives its hydrazone, b. p. 215—220°, which when hydrogenated gives almost exclusively the primary amine, *m*-methyl*cyclo*hexylamine, b. p. 152°/750 mm.; d_4^{21} 0.8956, giving a *phenylcarbamide*, m. p. 145°. *p*-Methyl*cyclo*hexanone gives its hydrazone, b. p. 215°, and its ketazine, b. p. 280—285°. The mixture of these two substances on hydrogenation yields *p*-methyl*cyclo*hexylamine, b. p. 153°/750 mm.; d_4^{20} 0.9057 (giving a *hydrochloride*, m. p. 245°), together with some *di*-*p*-methyl*cyclo*hexylamine, b. p. 275—278°, giving a *hydrochloride*, m. p. 198°. In all cases, a very good yield of the primary amine is obtained and only a small amount of the secondary amine. W. G.

The Dinitrotoluidines. OSCAR LISLE BRADY, JAMES NELSON EDMUND DAY, and WILLIAM JOSEPH WOODGATE ROLT (T., 1922, **121**, 526—532).

***p*-Cymene.** III. The Bromination of 2-Amino-*p*-cymene. ALVIN S. WHEELER and IRA W. SMITHEY (*J. Amer. Chem. Soc.*, 1921, **43**, 2611—2618).—2-Acetyl-amino-*p*-cymene on bromination in carbon tetrachloride solution yields 3(?)*-bromo*-2-acetyl-amino-*p*-cymene, $C_8H_8MePrBrNHAc$, m. p. 122.5°. When hydrolysed with concentrated hydrochloric acid, it yields 3(?)*-bromo*-2-amino-*p*-cymene, b. p. 169—170°/20 mm.; d_4^{21} 1.30125; n_D^{20} 1.5781, giving a *hydrochloride*, m. p. 205—210° (decomp.), and a *hydrobromide*, m. p. 200—203° (decomp.). In an endeavour to establish the position of the bromine atom in the ring, the acetyl derivative was oxidised with neutral permanganate, 3(?)*-bromo*-2-acetylaminotoluic acid, m. p. 215°, being obtained, which on hydrolysis gave 3(?)*-bromo*-2-aminotoluic acid, m. p. 151°, in the form of its *hydrochloride*, m. p. 190° (decomp.). This bromoaminotoluic acid is not identical with the only one known, namely, 5-bromo-2-amino-*p*-toluic acid, m. p. 186—187°, and hence the bromine must be in position 3 or 6, and the authors prefer the position 3 as representing an ortho-compound.

3-Bromo-2-amino-*p*-cymene can be diazotised and the product

coupled with the original base or other amines, and the following compounds are described: 2-Diazoamino-3-bromo-*p*-cymene, m. p. 143–146° (decomp.); 2-benzenediazoamino-3-bromo-*p*-cymene, m. p. 152–154° (decomp.), giving a hydrochloride, m. p. 161–162° (decomp.); 2-*p*-nitrobenzenediazoamino-3-bromo-*p*-cymene, has m. p. 158° (decomp.). On reversing the process in the last case by diazotising the *p*-nitroaniline and adding the bromoaminocymene, a product, m. p. 163° (decomp.), is obtained. These compounds of *p*-nitroaniline are yellow and dissolve in alkaline solutions, with the formation of a rich magenta colour which disappears when the solution is acidified. There is thus probably formed a pseudo or nitronic acid (cf. Hewitt and Mitchell, T., 1907, 91, 1254).

In the purification of *p*-cymene, isolated from spruce turpentine, itself a by-product in the manufacture of paper by the sulphite process, it is necessary in addition to the steps previously given (cf. A., 1920, i, 751) to extract the cymene with a limited amount of concentrated sulphuric acid or it acquires a yellow colour on keeping and does not behave satisfactorily when nitrated or brominated.

W. G.

Derivatives of Aminodiphenyl. A. GARCÍA BANÚS and JUAN FERRER TOMÁS (*Anal. Fís. Quím.*, 1921, 19, 293–312).—4-Dimethylaminodiphenyl (García Banús, *ibid.*, 1914, 12, 173), m. p. 119–120°, is prepared by alternate addition of methyl sulphate and 30% sodium hydroxide solution to aminodiphenyl in aqueous solution. By the action of sodium nitrite on the preceding compound in dilute hydrochloric acid solution at –5°, 3-nitro-4-dimethylaminodiphenyl is obtained, m. p. 119–120°. It forms large, garnet-red, monoclinic crystals [$a : b : c = 1.111 : 1 : 1.0961$, $\beta = 90^\circ 16' 30''$]. A secondary derivative is also obtained in small quantity, colourless crystals, m. p. 112–115°. By passing hydrogen chloride into an ethereal solution of the nitroamine, the hydrochloride is obtained in white, silky crystals, unstable apart from their mother-liquors. Nitration of dimethylaminodiphenyl gives the 3-nitro-derivative at first, but by further nitration a compound crystallising in large, colourless needles, is obtained, m. p. 122°. It is probably 3:5:2':4'-tetranitro-4-dimethylaminodiphenyl. Reduction of the 3-nitro-derivative gives 3-amino-4-dimethylaminodiphenyl; it forms silky crystals, m. p. 59–60°; b. p. 200°/15 mm. By reduction of 4-nitro-3-aminodiphenyl, 3:4-diaminodiphenyl is obtained in grey plates, m. p. 102–103°. The action of nitrous acid on dimethyl anilines containing a negative group in the para position is discussed.

G. W. R.

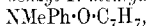
Hydrogenation by Formic Acid of some Quaternary Salts of Hexamethylenetetramine. MARCEL SOMMELET and JEAN GUIOTH (*Compt. rend.*, 1922, 174, 687–689).—When hexamethylenetetramine benzylechloride is warmed with formic acid, it undergoes hydrogenation, carbon dioxide is liberated, and one of the principal products is benzyldimethylamine. With other quaternary salts of the tetramine, the yields depended on the nature of the salt.

Thus acyclic derivatives of the type of the ethiodide or the *n*-butiodide, or salts like the phenylpropiodide gave very poor yields. On the other hand, substituted benzyl salts such as the *p*-ethylbenzylchloride gave satisfactory yields, but in such cases there was a secondary reaction producing benzaldehyde. W. G.

Behaviour of Allyl- and Benzyl-amino-oxides towards Sodium Hydroxide Solution. JAKOB MEISENHEIMER, HELLMUTH GREESKE, and AMALIE WILLMERSDORF (*Ber.*, 1922, 55, [B], 513—522).—The rearrangement of methylallylaniline *N*-oxide to *N*-phenyl-*N*-methyl-*O*-allylhydroxylamine (A., 1920, i, 35) is reproduced by ethylallylaniline *N*-oxide, and by benzylmethylaniline oxide, but not by dialkylallylamino-oxides.

[H. GREESKE.]—Ethylallylaniline *N*-oxide, characterised by its *picrate*, $C_{11}H_{15}ON, C_6H_3O_7N_3$, granular crystals, m. p. 120—122°, is converted by aqueous sodium hydroxide into *N*-phenyl-*N*-ethyl-*O*-allylhydroxylamine, $NMePh \cdot O \cdot C_3H_5$, a yellow oil, b. p. 104°/15—16 mm.

[A. WILLMERSDORF.]—Diethylallylamine, b. p. 105—113°, is obtained from diethylamine and allyl bromide; its *picrate*, $C_7H_{15}N, C_6H_3O_7N_3$, forms irregular prisms, m. p. 94—95°. Diethylallylamine oxide *picrate*, $C_7H_{15}ON, C_6H_3O_7N_3$, crystallises in needles or prisms, m. p. 138°. Dimethylallylamine, best prepared by the process of Partheil and von Broich (A., 1897, i, 263), furnishes an oxide, of which the *picrate*, $C_5H_{11}N, C_6H_3O_7N_3$, forms dark yellow needles, m. p. 136°. Benzylmethylaniline (Wedekind, A., 1899, i, 351), yields a *picrate*, $C_{14}H_{15}N, C_6H_3O_7N_3$, prisms, m. p. 127°, and an oxide (*picrate*, $C_{14}H_{15}ON, C_6H_3O_7N_3$, yellow prisms, m. p. 130°); it suffers rearrangement by alkali hydroxide to *N*-phenyl-*O*-benzyl-*N*-methylhydroxylamine,



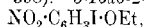
a yellow oil, soluble in cold concentrated hydrochloric acid, and reprecipitated on dilution. J. K.

cycloHexene Oxide and o-Methylcyclohexanol. MARCEL GODCHOT and PIERRE BÉDOS (*Compt. rend.*, 1922, 174, 461—464).—cycloHexene is quantitatively oxidised in chloroform solution by perbenzoic acid to cyclohexene oxide. The oxide behaves towards magnesium methyl iodide in exactly the same manner as does ethylene oxide itself, the product being *o*-methylcyclohexanol. This alcohol, although having the same b. p., 163—164°, as has the methylcyclohexanol obtained by Sabatier and Mailhe (cf. A., 1905, i, 275) by the hydrogenation of cresol, is apparently not the same alcohol, but a position isomeride. It gives a *phenylurethane*, m. p. 81—82°, and a *hydrogen phthalate*, m. p. 99—100°. The alcohol obtained from cresol gives a *phenylurethane*, m. p. 104°, and a *hydrogen phthalate*, m. p. 117—118°. The two alcohols are apparently *cis-trans* isomerides. W. G.

Solubilities and Cooling Curves of the Mononitrophenols. L. L. CARRICK (*J. Physical Chem.*, 1921, 25, 628—659).—The various equations for calculating the solubility have been applied

to the solubility of the three nitrophenols and found to be unsuitable for calculating the solubility of these substances in acetone, benzene, ethyl alcohol, or ethyl ether. The solubility of the three isomerides has been determined in the solvents named at a series of temperatures over the range 0—104.2°. Many of the determinations at the higher temperatures were carried out in sealed tubes. The experimental values have been compared with those calculated by Findlay's equation, $R = R' + C(t' - t)$ (A., 1902, ii, 386), and by Hildebrand's equation, $\log N = -L(T_m - T)/4.58T \cdot T_m$ (A., 1916, ii, 518; 1918, ii, 36, 65); the agreement is not good in either case, but is considerably better in the case of the former equation than in the latter. Cooling curves have been determined for the three binary systems made up of pairs of the mono-nitrophenols, and also for the systems made up of the eutectics from each binary system and the third nitrophenol. In the system *o*-nitrophenol-*p*-nitrophenol, the eutectic lies at 34.5° and has a composition 27% of the para constituent; the system *o*-nitrophenol-*m*-nitrophenol has a eutectic at 31.5° with 70% of *o*-nitrophenol; the system *m*-nitrophenol-*p*-nitrophenol gives a eutectic at 61° having a composition 45.5% of *p*-nitrophenol. The melting points of the various mixtures have been calculated by means of the Le Chatelier and van Laar equation, $\log \alpha = -L(T_0 - T)/(RT_0T)$, and found to be in good agreement with the observed values. It is shown that this law may be used equally well for calculating the cooling curves of ternary mixtures. The mononitrophenols in the presence of one another behave as ideal solutions. Benzene is shown to be a good solvent for the extraction of *o*-nitrophenol from aqueous solutions of the mixed mononitrophenols. J. F. S.

Nitration of 5-Iodo-2-nitrophenetole. C. APOSTOLO (*Gazzetta*, 1921, 51, ii, 396—398).—5-Iodo-2-nitrophenetole,



obtained by the action of concentrated potassium hydroxide solution on alcoholic 5-iodo-1:2-dinitrophenetole solution, forms crystals, m. p. 86—87°. When treated with fuming nitric acid at the ordinary temperature, it yields 5-iodo-2:4-dinitrophenetole (or 5-iodo-2:6-dinitrophenetole), $\text{OEt-C}_6\text{H}_2\text{I(NO}_2)_2$, which crystallises in lustrous, pale yellow needles, m. p. 111—112°. T. H. P.

The Nitration of Halogenated Phenols. I. CHAS. RAIFORD (*J. Amer. Chem. Soc.*, 1922, 44, 158—163; cf. Upson, A., 1904, i, 734; Zincke and Hedenström, A., 1907, i, 124).—When 3:5-dibromo-*o*-cresol is nitrated by the action of sodium nitrite on its solution in glacial acetic acid, 5-bromo-3-nitro-*o*-cresol, m. p. 90—91° (cf. Upson, *loc. cit.*), and 3-bromo-5-nitro-*o*-cresol, m. p. 120° (decomp.) (cf. Robertson, T., 1908, 93, 788), are obtained. When 3-bromo-5-nitro-*o*-cresol is reduced by stannous chloride and hydrochloric acid, it yields 3-bromo-5-amino-*o*-cresol, m. p. 142° (decomp.), isolated as its hydrochloride. The hydrochloride when warmed with acetic anhydride and anhydrous sodium acetate yields 3-bromo-5-acetyl-amino-2-acetyl-toluene, m. p. 169°.

which with cold aqueous sodium hydroxide gives 3-bromo-5-acetyl-amino-o-cresol, m. p. 154–155°. The amino-hydrochloride described above, when oxidised with ferric chloride, gives 3-bromo-2:5-toluquinone (cf. Claus and Jackson, A., 1889, 128). 5-Bromo-3-nitro-o-cresol, like its isomeride, when reduced yields 5-bromo-3-amino-o-cresol, m. p. 113°, giving a hydrochloride, which on acetylation yields 5-bromo-3-acetylamino-2-acetoxyltoluene, m. p. 199–200°. W. G.

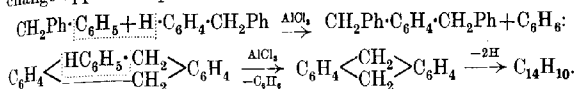
[Tautomerism of Resorcinol.] W. FUCHS (*Ber.*, 1922, 55, [B], 491–492).—Polemical (cf. Fuchs and Elsner, A., 1920, i, 545; 1921, i, 241; Herzig and Zeisel, A., 1920, i, 732). H. W.

Elimination of Hydrogen from Aromatic Nuclei and Union of the Latter by means of Aluminium Chloride. VI. Experiments with Phenol-ethers and with Diphenylmethane. ROLAND SCHOLL and CHRISTIAN SEER (*Ber.*, 1922, 55, [B], 330–341; cf. this vol., i, 258).—Elimination of hydrogen and union of the aryl residues occur with particular ease in the cases of α -naphthyl alkyl ethers, less readily with the corresponding β -naphthyl ethers, and, according to preliminary experiments, to a very restricted extent with phenolic ethers. Reaction is effected in the presence of nitrobenzene and there can be no doubt but that the latter exercises a specific influence probably by saturating the subsidiary valencies of the carbon of the aromatic nucleus, and thus rendering the hydrogen atom mobile and also by utilisation of the eliminated hydrogen. The aluminium chloride appears to have the dual function of activating the aromatically combined hydrogen atom and also the nitro-group of nitrobenzene, probably by the formation of readily dissociable molecular compounds.

4:4'-Diethoxy-1:1'-dinaphthyl, colourless, lustrous leaflets, m. p. 212–213°, is prepared in 70% yield by the gradual addition of anhydrous aluminium chloride to a solution of α -naphthyl ethyl ether in anhydrous benzene at the atmospheric temperature; hydrogen chloride is not thereby evolved. The same substance is obtained when ethyl chloroformate is added to the mixture, thus showing that the union of the naphthyl residues occurs with much greater rapidity than the fission of the ester. 4:4'-Dimethoxy-1:1'-dinaphthyl crystallises in colourless, lustrous needles, m. p. 252–253°. 2:2'-Dimethoxy-1:1'-dinaphthyl, m. p. 190–191°, and diresorcinyl tetramethyl ether, long, brown needles, m. p. 124°, are also described.

[With HEINRICH NEUMANN.]—The behaviour of aromatic hydrocarbons having mobile hydrogen atoms towards aluminium chloride has also been investigated. Anthracene and phenanthrene are very readily attacked in the presence of nitrobenzene, but the isolation of homogeneous products of the reaction has not been found possible. On the other hand, diphenylmethane reacts readily with aluminium chloride at the atmospheric temperature and in the absence of solvent without formation of resinous products; in this case, however, union of the benzene nuclei does not occur,

benzene and anthracene being the only substances isolable. The change appears to proceed in accordance with the scheme :



The isolation of *o*- or *p*-dibenzylbenzene which are presumed to be formed intermediately has not been effected. On the other hand, it is shown that *mesodihydroanthracene* is dehydrogenated by aluminium chloride at the atmospheric temperature to anthracene, probably with simultaneous formation of a corresponding quantity of more fully hydrogenated products, and that anthracene readily yields a molecular compound with aluminium chloride (cf. Lavaux and Lombard, A., 1910, i, 548). H. W.

Catalytic Preparation of cycloHexanetriols. J. B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1922, **174**, 616—618).—*cycloHexanetriols* may readily be prepared by catalytic reduction in the presence of nickel in alcohol or water at about 140° under pressure of the corresponding trihydroxybenzenes (cf. this vol., i, 136). Under these conditions, pyrogallol gives a mixture of two isomeric *cyclohexane-1:2:3*-triols, of which one has m. p. 145°, b. p. 290°, and gives a triacetate, m. p. 47°, b. p. 288°, and the other has m. p. 95°, b. p. 225°, and gives a triacetate, b. p. 238°. Under similar conditions, phloroglucinol gives a mixture of isomeric *cyclohexane-1:3:5*-triols, b. p. 245—260°; and *1:2:4*-trihydroxybenzene gives a mixture of isomeric *cyclohexane-1:2:4*-triols, b. p. 260—280°. W. G.

The Transfer of Hydrogen from an Alcohol to an Aldehyde. C. H. MILLIGAN and E. EMMET REID (*J. Amer. Chem. Soc.*, 1922, **44**, 202—205).—By passing the vapours of an aldehyde mixed with ethyl alcohol over cerium oxide at 300—380°, the aldehyde is hydrogenated to the corresponding alcohol and the ethyl alcohol oxidised to acetaldehyde. In this way, benzyl, phenylethyl, and heptyl alcohols and citronellol have been prepared from the corresponding aldehydes. The yields are low and the life of the catalyst is short as it becomes foul owing to the production of gummy products, probably arising from the condensation of the aldehydes. If the cerium oxide is replaced by copper on an inert support benzaldehyde is reduced to toluene. W. G.

Phenyldi- α -naphthylcarbinol and Phenyldi- α -naphthylmethyl. C. S. SCHOEPFLE (*J. Amer. Chem. Soc.*, 1922, **44**, 188—194; cf. Gomberg and Schoepfle, A., 1917, i, 551; 1920, i, 26).—Phenyldi- α -naphthylcarbinol (cf. Elbs, A., 1887, 943) is best prepared by the interaction of ethyl benzoate and magnesium α -naphthyl bromide in toluene at 110—115°. The carbinol has m. p. 166—167° and gives additive compounds with ether, ethyl acetate, acetone, and ethyl alcohol of the type $\text{C}_{27}\text{H}_{20}\text{O}\cdot\text{EtOH}$, and with benzene, $2\text{C}_{27}\text{H}_{20}\text{O}\cdot 3\text{C}_6\text{H}_6$. With acetyl chloride, it

yields phenyldi- α -naphthylchloromethane, m. p. 165–167° (decomp.), and with acetyl bromide phenyldi- α -naphthylbromomethane, m. p. 125–127° (decomp.). Both these compounds give additive compounds with mercuric, stannic, ferric, aluminium, and zinc chlorides, all of which are unstable, decomposing in a short time to give phenyldi- α -naphthylfluorene, which was also obtained by boiling an acetic acid solution of phenyldi- α -naphthylcarbinol. Phenyldi- α -naphthylmethane, m. p. 204° (cf. Elbs, *loc. cit.*) was prepared by reducing the carbinol with zinc dust and acetic acid at 75–80°. Phenyldi- α -naphthylmethyl was obtained by shaking a benzene solution of the above chloromethane with molecular silver in the absence of air. It was very unstable and could only be obtained in solution. It readily undergoes auto-reduction, giving phenyldi- α -naphthylmethane and phenyldi- α -naphthylfluorene. It also absorbs oxygen, but attempts to prepare a peroxide were not successful. With hydrochloric acid in the absence of air, it gives phenyldi- α -naphthylmethane and phenyldi- α -naphthylchloromethane. W. G.

Influence of Substitution in the Ortho-, Meta-, and Para-positions on the Absolute Affinity of Benzoic Acid. I. H. N. K. RØRDAM (*Z. physikal. Chem.*, 1921, **99**, 474–498).—The absolute affinities (free energy changes) between silver oxide and benzoic, *o*-, *m*-, and *p*-toluic acids, and cinnamic acid, were measured by an electromotive method. Silver oxide exists in two modifications: (a) the electrolytically precipitated oxide, unstable at the ordinary temperature but stable at higher temperatures; (b) the ordinary precipitated oxide, stable at the ordinary temperature but unstable at higher temperatures. The transition temperature was calculated as 132°. The affinity of benzoic acid is reduced by the introduction of methyl into the benzene nucleus, the effect being greatest in the *o*-position. The effects in the *m*- and *p*-positions were weaker and approximately equal. The absolute affinity of cinnamic acid towards silver oxide is 37% greater than that of benzoic acid, whereas the conductivity measurements would, on the assumption that the strength is proportional to the ionisation, make benzoic acid almost twice as strong as cinnamic acid. The *E.M.F.* of the oxy-hydrogen cell was calculated as 1.227 volts at 25°, in agreement with the results of Nernst and Wartenberg and of Brönsted. The lower value calculated by Lewis arises from the fact that the dissociation pressures of silver oxide, measured at higher temperatures, referred to one form, whilst the *E.M.F.* measurements, carried out at lower temperatures, referred to the second form, of silver oxide. If account is taken of this, all the results are in agreement. A method for the determination of hydrogen ions is indicated. J. R. P.

The Reduction of Ethyl Benzoate and some other Benzene Derivatives by Sodium and Absolute Alcohol. HÉRVÉ DE POMMEREAU (*Compt. rend.*, 1922, **174**, 685–687).—When ethyl benzoate is reduced by sodium in absolute alcohol, the main product is cyclohexanecarboxylic acid together with a little cyclo-

hexylcarbonyl alcohol, b. p. 188°/760 mm., giving a *urethane*, m. p. 63°. Under similar conditions, benzaldehyde gives toluene and *cyclohexanecarboxylic acid*, but phenol, phenetole, and aniline do not undergo reduction. Nitrobenzene gives aniline with a little hydrazobenzene. W. G.

Solubility of the Isomeric Toluic Acids in the Three Xylenes. CHAPAS (*Compt. rend.*, 1922, 174, 610—611).—The solubilities of the three toluic acids in the three xylenes expressed as grams of the acid dissolved in 100 grams of the xylene at 14° are :—

	<i>o</i> -Xylene.	<i>m</i> -Xylene.	<i>p</i> -Xylene.
<i>o</i> -Toluic acid	7.11	5.78	7.39
<i>m</i> -Toluic acid	8.63	8.57	10.32
<i>p</i> -Toluic acid	1.05	0.91	1.47

W. G.

The Action of Light on the Cinnamic Acids and the Constitution of the Truxillic Acids. A. W. K. DE JONG (*Ber.*, 1922, 55, [B], 463—474).—During recent years, a number of papers on these subjects have been published by Stobbe and Störmer, in which the author's work has not been taken into account; the latter is now published in a more extended form.

The conversion of *allocinnamic* into β -truxillic acid is preferably effected by the action of direct sunlight on the cooled acid; the presence of benzoic, α - or β -truxillic acids in the *allo*-acid is inhibitive, whereas that of *trans*-cinnamic acid is highly favourable. Further experiment shows that *trans*-cinnamic acid can form α - and β -truxillic acids, that the production of β -truxillic acid from *allocinnamic* acid does not take place directly but indirectly through the *trans*-acid and that β -truxillic acid is not formed by the union of molar quantities of the *allo*- and *trans*-acid. Illumination of non-recrystallised *trans*-cinnamic acid yields solely α -truxillic acid, but, if illumination is interrupted and the acid is recrystallised, β -truxillic acid is produced to a greater or less extent. The latter acid appears to be produced from β -cinnamic acid, which is readily formed by pouring a solution of the α -acid in alcohol, nearly saturated at the atmospheric temperature, into a large volume of water or by dissolving the α -acid in ammonia and adding an excess of hydrochloric acid to the solution. It may be noted that *allo*-, α -, and β -cinnamic acids are not converted into truxillic acids by exposure to red, yellow, or green light.

Stobbe and Störmer have observed the production of β -truxillic acid, but seldom of α -truxillic acid, when *allocinnamic* acid is illuminated, whereas the author has found that the α -acid is formed in considerable quantity; the discrepancy is to be ascribed to the differing temperatures used during the experiment, rise in temperature favouring the formation of the α -acid.

The presence of δ -truxillic and β -cocaic acids in the natural truxillic acid (Störmer, A., 1921, i, 179) has been established previously by the author (A., 1911, ii, 552).

The constitutions assigned to α -, γ -, δ -, and ϵ -truxillic acids by

Störmer and Förster (A., 1919, i, 444) are in agreement with those proposed previously by de Jong (A., 1918, i, 172), but this is not the case with β -truxillic and β -cocaic acids.

Störmer's proposal (A., 1921, i, 179) to divide the acids into the truxillic and truxinic series is criticised adversely; it appears preferable to retain the original names until the structure of the compounds is definitely elucidated. H. W.

Preparation of *ar*-Tetrahydronaphthylthiolacetic Acids. TETRALIN G. M. B. H. (Brit. Pat. 148419).—Tetrahydronaphthalene is sulphonated with chlorosulphonic acid at a temperature not exceeding 5° ; the resulting sulphonyl chlorides are reduced with zinc dust and hydrochloric acid to a mixture of 1- and 2-tetrahydronaphthylthiols, and after purification by distillation under reduced pressure (b. p. $143-147^{\circ}/15$ mm.) they are condensed in alkaline solution with monochloroacetic acid with the formation of 1- and 2-tetrahydronaphthylthiolacetic acids, $C_{10}H_{11}S\cdot CH_2\cdot CO_2H$. The two acids are separated by adding a concentrated ammonium chloride solution to the reaction mixture when the ammonium salt of the 2-acid separates in crystalline flakes. From the mother-liquors, the 1-acid is precipitated with hydrochloric acid as a voluminous, white precipitate, which after crystallisation from benzene melts at $133-135^{\circ}$. The 2-acid, precipitated from the solution of its ammonium salt, melts at $69-70^{\circ}$. Both acids are easily converted into "tetrahydronaphthylthioindigo."

G. F. M.

Friedel and Crafts' Reaction. Some Substituted Phthalic Anhydrides with Toluene and Aluminium Chloride. WALTER

A. LAWRENCE (*J. Amer. Chem. Soc.*, 1921, 43, 2577—2581; cf. A., 1920, i, 741).—When toluene is condensed with unsymmetrical phthalic anhydrides in the presence of aluminium chloride, it gives, in some cases, two acid products and in others only one. The physical properties of the toluoylnitrobenzoic acids are very similar to those of the benzoylnitrobenzoic acids (*loc. cit.*).

With 3-nitrophthalic anhydride, toluene gives 2-nitro-6-*p*-toluoylbenzoic acid, m. p. $262-265^{\circ}$ (decomp.), and 3-nitro-2-*p*-toluoylbenzoic acid, m. p. $123-126^{\circ}$ (decomp.). With 4-nitrophthalic anhydride, the products are 4-nitro-2-*p*-toluoylbenzoic acid, m. p. $101-105^{\circ}$ (decomp.), and a small amount of a compound, m. p. $211-218^{\circ}$ (decomp.). With 3-acetylaminophthalic anhydride, the products are two *p*-toluoylaminobenzoic acids, m. p. $256-257^{\circ}$ and 206° , respectively, in which the toluoyl group is, in each case, in position 2 or 6 and the amino-group in position 3 or 2. With 4-acetylaminophthalic anhydride, practically the whole of the yield consisted of one *p*-toluoylaminobenzoic acid, m. p. $135-136^{\circ}$, the toluoyl group being in position 2 or 6 and the amino-group in position 4 or 3. A small amount of an unidentified compound, m. p. $180-183^{\circ}$, was also obtained. Tetrachlorophthalic anhydride gave with toluene 2 : 3 : 4 : 5-tetrachloro-6-*p*-toluoylbenzoic acid, m. p. $174-175^{\circ}$ (corr.) (cf. 1914, Brit. Pat. 8917), giving a methyl ester, m. p. $96-97^{\circ}$ (corr.).

Tetrabromophthalic anhydride gave 2:3:4:5-tetrabromo-6-*p*-toluoylbenzoic acid, m. p. 212° (corr.), giving a methyl ester, m. p. 162.5° (corr.); and tetraiodophthalic anhydride gave 2:3:4:5-tetraiodo-6-*p*-toluoylbenzoic acid, m. p. 266° (corr.), giving a methyl ester, m. p. 199° (corr.). W. G.

Homogentisic Acid. II. The Behaviour of Homogentisic Acid when Boiled with Ferric Chloride. CARL TH. MÖRNER (*Z. physiol. Chem.*, 1921, **117**, 67—84; cf. A., 1912, i, 459).—When homogentisic acid is distilled with a concentrated solution of ferric chloride, the distillate contains a substance which crystallises in leaflets, m. p. 89–90°, and when heated on the water-bath sublimates, yielding thin, broad, iridescent needles. S. S. Z.

Homogentisic Acid. III. CARL TH. MÖRNER (*Z. physiol. Chem.*, 1921, **117**, 85–90).—Homogentisic acid crystallises with one molecule of water in monoclinic prisms. It forms a lactone at 130°, at which temperature it partly sublimates. At about 17.5°, its solubility in water is 1:1.8. S. S. Z.

Quinhydrones of the Maleic Anhydride Series. PAUL PFEIFFER [with E. FLATER] (*Ber.*, 1922, **55**, [B], 413–429).—In a previous communication (Pfeiffer and Böttler, A., 1919, i, 62), it has been shown that maleic anhydride and analogous substances give more or less deeply coloured solutions in hydrocarbons, phenols, amines, etc., although, in general, the isolation of the additive compounds in the solid state was not found possible. The close analogy of maleic anhydride to the quinones was thus demonstrated, and it was pointed out that the relationship between maleic anhydride and furan is the same as that between *p*-benzoquinone and benzene. The work has now been extended in a variety of directions which show that the presence of the group, $\text{CO}\cdot\overset{\cdot}{\text{C}}\cdot\text{CO}$, is necessary for the formation of quinhydrones and that it is largely a matter of indifference whether it is present in a closed ring, as in *p*-benzoquinone or maleic anhydride, or in an open chain, as in phthalaldehyde or *s*-phthalyl chloride. In particular, tetrahalogenated phthalic anhydrides exhibit a great power of forming solid additive products with many classes of compounds and are to be classed in this respect with *s*-trinitrobenzene and picric acid. The precise rôle of the halogen atoms has not been elucidated (cf. Pratt and Perkins, A., 1918, i, 167; Pratt and Young, A., 1918, i, 540). Since the anhydrides unite with aromatic hydrocarbons as well as with the corresponding phenols, amines, etc., it is evident that the compounds are formed by saturation of affinity between one or both oxygen atoms of the anhydride component and the unsaturated carbon atoms of the benzenoid component, thus $\text{C}_6\text{Cl}_4\text{C}_5\text{O}_3 \dots \text{C}_n\text{H}_m$.

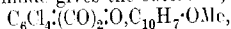
The following compounds are derived from tetrachlorophthalic anhydride, and contain the components in equimolecular ratio. In general, they are formed by allowing a solution of the requisite constituents in hot glacial acetic acid to cool slowly. With mesitylene, the substance $\text{C}_6\text{Cl}_4(\text{CO})_2\text{O}\cdot\text{C}_6\text{H}_3\text{Me}_3$, pale yellow needles which

evolve the hydrocarbon slowly at the atmospheric temperature; with naphthalene, greenish-yellow, silky needles; with 1-methylnaphthalene, greenish-yellow needles; with acenaphthene, golden-yellow, slender needles, m. p. 237—240°; with anthracene, golden-yellow, lustrous needles, m. p. 195°; with phenanthrene, long, yellow needles, m. p. 190°; with α -bromonaphthalene, pale yellow needles which dissociate when heated gently; with α -naphthol, orange-coloured, lustrous needles, m. p. 250°; with β -naphthol, small, yellow needles, m. p. 210°; with α -naphthyl ethyl ether, deep yellow needles which dissociate when heated gently; with β -naphthyl methyl ether, greenish-yellow needles which dissociate when heated; with diphenylene oxide, long, greenish-yellow, lustrous needles; with carbazole, yellow, lustrous needles, m. p. 210°.

Tetrachlorophthalic anhydride does not appear to unite with stilbene; its additive product with 2 : 4 : 5 : 2' : 4' : 5'-hexamethylstilbene has been described previously (Pfeiffer and Böttler, *loc. cit.*). Maleic anhydride does not give crystalline additive compounds with α -naphthyl ethyl ether or β -naphthyl methyl ether, and bromomaleic anhydride does not give solid products with β -naphthol or β -naphthyl methyl ether. Solid compounds were not prepared from phthalic anhydride and α -naphthyl ethyl ether, from tetrachlorophthalic anhydride and diphenylamine, or from phthalic anhydride and acenaphthene.

3 : 6-Dichlorophthalic anhydride gives a crystalline compound, with acenaphthene, $C_6H_2Cl_2(CO)_2 \cdot O \cdot C_{12}H_{10}$, lemon-yellow needles, m. p. 119—120°, but not with carbazole.

Tetrachlorophthalimide gives the substance,



lemon-yellow crystals with α -naphthyl methyl ether and a similar compound, small, lemon-yellow needles, with α -naphthyl ethyl ether; both substances lose the ethereal component when heated gently.

Tetrabromophthalic anhydride yields crystalline additive compounds with naphthalene, pale greenish-yellow needles, acenaphthene, long, dark yellow needles, and α -naphthyl ethyl ether, small, dark yellow needles; the compounds dissociate into their components when heated.

Chloranil and acenaphthene yield the substance, $C_6Cl_4O_2 \cdot C_{12}H_{10}$, black, lustrous needles.

Solid, additive compounds were not obtained from chloranil and fluorene, diphenylene oxide and carbazole, or 2 : 2'-dihydroxydiphenyl, from bromanil and acenaphthene, from 2 : 5-dichloroquinone and diphenylene oxide, β -naphthol, α -bromonaphthalene, or β -naphthyl methyl ether.

Phthalaldehyde gives an orange-yellow solution in dimethylaniline in which phthalide dissolves with development of colour; on the other hand, the solutions of the aldehyde and phthalide in concentrated sulphuric acid are colourless and pale greenish-yellow respectively.

Terephthalyl chloride gives a coloured solution in guaiacol or acenaphthene, whereas the similar solutions of isophthalyl chloride

are colourless. Both chlorides yield yellow solutions in dimethylaniline. H. W.

The Formation and Stability of *spiro*-Compounds. VII. The Application of the Dieckmann Reaction to Esters of the Glutaric Series. GEORGE ARMAND ROBERT KON (T., 1922, 121, 513—526).

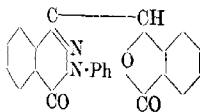
The Preparation and Properties of Several Phenylalkylsuccinic Acids. FRED W. UPSON and T. J. THOMPSON (*J. Amer. Chem. Soc.*, 1922, 44, 181—188).—Two methods are suggested for the preparation of phenylalkylsuccinic acids. In the first, alkyl cyanohydrins are condensed with benzyl cyanide by means of sodium methoxide or ethoxide (cf. Avery and Upson, A., 1908, i, 343) and in the second, the esters of α -bromo-fatty acids are condensed with benzyl cyanide by means of sodamide. The resulting nitriles are, in each method, saponified. The following new succinic acids are described: *Phenylmethylsuccinic acid*, $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, m. p. 182° ; *phenylethylsuccinic acid*, m. p. 196° ; *phenyl-n-propylsuccinic acid*, m. p. 213° ; and *phenyl-isobutylsuccinic acid*, m. p. 183.4° . In the second method of preparation, the intermediate product is in each case a half nitrile, half ester of the required succinic acid, the nitrile group being adjacent to the phenyl group. The complete hydrolysis of the nitriles or nitrile esters of phenylisopropyl- and phenylisobutylsuccinic acids cannot be brought about by the usual acid or alkali methods, but these substances must be heated in a sealed tube at 130 — 140° for from twenty-four to thirty hours.

It was found that when the sodium phenylacetone nitrile obtained by the action of sodamide on phenylacetone nitrile was left exposed to the air after the evaporation of the solvent ether, the material underwent vigorous auto-oxidation. From an examination of the products of this oxidation, the authors suggest that the constitution of this sodium derivative is best represented by $\text{CHPh}\cdot\text{C}\cdot\text{NNa}$.

W. G.

Stilbene-2 : 2'-dicarboxylic Acid. PAUL RUGGLI and R. ERNEST MEYER (*Helv. Chim. Acta*, 1922, 5, 28—59).—A number of derivatives of stilbene-2 : 2'-dicarboxylic acid have been examined with the object of preparing toluene-2 : 2'-dicarboxylic acid; the great readiness with which these substances pass into compounds containing the lactone ring has prevented the fulfilment of the original purpose.

Diphthalyl-lactonic acid, $\text{CO}\langle\text{C}_6\text{H}_4\rangle\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (cf. Reissert, A., 1913, i, 622), is prepared by the reduction of phthalic anhydride by zinc dust in neutral, aqueous-alcoholic solution and is characterised by its conversion by phenylhydrazine in alcoholic solution into 3-phenyl-1-phthalidophthalazone (annexed formula), colourless, silky needles, m. p. 207° . It is reduced by zinc dust in alkaline solution to hydrodiphthal-



lactonic acid, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{CH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, m. p. 198.5° (*methyl* ester, colourless needles, m. p. 115° , *ethyl* ester, m. p. 76° , *amide*, minute needles, m. p. $227-228^\circ$). Hydrodiphthalyl-lactonic acid is converted by potassium cyanide at $215-230^\circ$ into stilbene-2:2'-dicarboxylic acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, m. p. $263-265^\circ$, when heated rapidly.

[With P. HUBERT.]—The chlorination of stilbene-2:2'-dicarboxylic acid suspended in chloroform does not proceed uniformly; in addition to considerable quantities of resinous matter, a *substance*, possibly, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{CCl} \cdot \text{CHCl} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, m. p. 177° , is

formed. Sodium stilbene-2:2'-carboxylate is very readily brominated in aqueous solution, but the primary dibromide loses sodium bromide immediately and passes into hydrodiphthalyl, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{CH} \cdot \text{CH} \langle \text{C}_6\text{H}_4 \rangle \text{CO}$, m. p. $255-257^\circ$ after softening

at 240° . In the hope of avoiding ring closure, the behaviour of the esters of stilbene-2:2'-dicarboxylic acid towards halogens has been examined (the diethyl ester has m. p. $79-80^\circ$, the *ethyl hydrogen* ester, m. p. $138-139^\circ$, and the *dimethyl* ester, long, colourless needles, m. p. $101-102^\circ$). The methyl ester combines very readily with chlorine, but, even at 0° , the primary product loses methyl chloride and passes into the *methyl* ester of *chlorohydrophthalyl-lactonic acid*, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{CH} \cdot \text{CHCl} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$, coarse, glassy crystals, m. p. $136.5-137.5^\circ$. In a similar manner, the ethyl ester gives *ethyl chlorohydrophthalyl-lactonate*, colourless rods, m. p. 143° . The methyl ester is converted by a molecular proportion of potassium hydroxide in alcoholic solution into *methyl benzylidenephthalide-o-carboxylate*, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$, colourless needles, m. p. $123.5-125^\circ$ (*dibromide*, m. p. $221-222^\circ$), which is converted by an excess of potassium carbonate into deoxybenzoin-2:2'-dicarboxylic acid (the latter may be similarly prepared directly from the chloro-ester). Ethyl stilbene-2:2'-dicarboxylate is converted by bromine in carbon tetrachloride solution into the *dibromide*, m. p. 162° , but the corresponding *compound*, m. p. 198° (decomp.), from the methyl ester is obtained in better yield; in the latter case, elimination of methyl bromide occurs to some extent with the formation of the *methyl* ester of bromohydrodiphthalyl-lactonic acid, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{CH} \cdot \text{CHBr} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$, m. p. 133° . The latter loses hydrogen bromide when heated somewhat above its melting point and yields a *compound*, $\text{C}_{17}\text{H}_{12}\text{O}_4$ (probably methylhydrodiphthalyl, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{CH} \cdot \text{CMc} \langle \text{C}_6\text{H}_4 \rangle \text{CO}$), which appears to pass under the influence of alkali into *methyldeoxybenzoin-2:2'-dicarboxylic acid*, m. p. $275-277^\circ$.

The behaviour of the normal dibromides of the stilbene-2:2'-dicarboxylic esters towards alkalis and amines has been examined. With one, two, or four molecular proportions of alcoholic potash,

the ester groups are hydrolysed and potassium salts of brominated acids are produced which are protected against further action by their insolubility. Reaction proceeds most smoothly when an excess of potassium carbonate is used in boiling aqueous-alcoholic solution and then leads to the formation of deoxybenzoin-2:2'-dicarboxylic acid which has m. p. 193° (decomp.) after softening at 180°, and, after resolidification, m. p. 222–245° (indefinite) after softening at 216°. (The acid is characterised further by its transformation into 3-phenyl-1-o-carboxybenzylphthalazone, colourless needles, m. p. 206°, and 3-carbamido-1-o-carboxybenzylphthalazone, pale yellow needles, m. p. [indefinite] 232°, to a red liquid.) With four molecular proportions of sodium ethoxide, the ester dibromides give the sodium salts of a mixture of acids which can only be separated from one another with considerable difficulty, in part owing to the ease with which some of them pass into lactones; it was found possible, however, to isolate deoxybenzoin-2:2'-dicarboxylic acid and an acid, m. p. 250°, which gave analytical results in agreement with those required by tolane-2:2'-dicarboxylic acid (the amount obtained was too small to permit further investigation). Pyridine causes the removal of bromine from stilbene-2:2'-dicarboxylic ester bromides with re-formation of the parent stilbene-2:2'-dicarboxylic esters; triethylamine has a similar effect at 170°. Since, according to Pfeiffer (A., 1912, i, 618), this behaviour is characteristic of the α -stilbenedibromides, and in the present instance it was not found possible to isolate the second isomerides, it appeared useless to study the bromides further, and the work was therefore continued with the dichlorides, attempts to avoid the undesired ring closure observed with the methyl and ethyl esters (see above) being made by suitable substitution in the carboxyl groups.

Amyl stilbene-2:2'-dicarboxylate, colourless, matted needles, m. p. 60–62°, yields resinous substances when treated with chlorine; amyl chloride is thereby eliminated. *Phenyl stilbene-2:2'-dicarboxylate*, transparent prisms, m. p. 206°, does not give crystalline chloro-derivatives; the corresponding *dibromide*, colourless granules, m. p. 222° (decomp.), is decomposed with difficulty by pyridine with regeneration of the parent ester. *Stilbene-2:2'-dicarboxyl chloride*, pale yellow needles, m. p. 159°, is prepared from the acid and thionyl chloride; in spite of its relative stability towards water, it appears to have the symmetrical structure. When chlorinated in the presence of warm chloroform, it gives 7:7'-dichlorostilbene-2:2'-dicarboxyl chloride, which is isolated in the form of the corresponding *methyl ester*, $C_{18}H_{14}O_4Cl_2$, colourless crystals, m. p. 183°; in cold solution, the methyl ester of chlorohydrodiphthalyl-lactonic acid is the main product of the change. Stilbene-2:2'-dicarboxyl chloride is transformed by ammonia into the *di-amide*, small, colourless crystals, m. p. 319°, by aniline into the *di-anilide*, m. p. 299°, and a *substance*, $C_{16}H_8O_4Cl$, long, slender needles, m. p. 263°, by methylaniline into the *di-methylanilide*, m. p. 175°, and a *product*, probably $C_6H_4 \begin{smallmatrix} CH \\ \diagup \diagdown \\ CO \end{smallmatrix} C \cdot C_6H_4 \cdot NMePh$, m. p. 196°, and by *p*-bromomethylaniline into the *di-p-bromo-*

methylanilide, $C_{30}H_{34}O_2N_2Br_2$, a colourless, crystalline powder, m. p. 200° ; the latter substance gives additive products with a molecular proportion of benzene or ethyl alcohol, m. p. 167° and 104° , respectively. Treatment of the nitrogenous compounds with chlorine gives resinous products.

The action of phosphorus pentachloride on deoxybenzoin-2:2'-dicarboxylic acid and subsequent treatment of the initial product with methyl alcohol, leads to the isolation of methyl benzylidene-phthalide-*o*-carboxylate instead of the desired 7-chlorostilbene-2:2'-dicarboxyl chloride.

4-Nitro-2-cyanotoluene, m. p. 105° , is condensed with benzaldehyde to 4-nitro-2-cyanostilbene, which is converted by bromine in carbon tetrachloride solution into 4-nitro-2-cyanostilbene di-bromide, colourless needles, m. p. $195-197^\circ$. The latter is transformed by pyridine or potassium carbonate into 4-nitro-2-cyanostilbene, by sodium ethoxide into resinous products. H. W.

Bile Salts. X. The Further Degradation of Deoxycholic Acid. HEINRICH WIELAND and WILHELM SCHULENBURG (*Z. physiol. Chem.*, 1921, **114**, 167-191; cf. A., 1921, i, 112, 113, 178).—To prepare the ketotricarboxylic acids, $C_{23}H_{34}O_7$, pyrocholoidanic acid is dissolved in alkali hydroxide in the cold and after thirty minutes the solution is made acid to Congo red with hydrochloric acid. The precipitate contains a mixture of the two isomerides. The β -acid is obtained by extracting the precipitate with ether and by further extracting the ethereal solution with alkali and acidifying. The β -acid crystallises as the hydrate, m. p. $110-115^\circ$. The anhydrous acid after crystallisation has m. p. $180-185^\circ$, and $[\alpha]_D^{25} -56.3^\circ$ in alcohol. The same pyrocholoidanic acid is obtained from it as from the α -acid. *Prosolanellitic acid*, $C_{23}H_{34}O_6$, is obtained by dissolving the α -ketotricarboxylic acid in alkali hydroxide, oxidising with potassium permanganate, and precipitating with acid. The hydrated acid crystallises in spherical aggregates of lustrous needles, m. p. 220° , but on exposure in a vacuum it loses 3.45% of water and then has m. p. 180° , $[\alpha]_D^{25} +75.5^\circ$ in alcohol. *Pyroprosolanellitic acid*, $C_{22}H_{30}O_6$, prepared from prosolanellitic acid by distillation in a vacuum at 300° , crystallises in colourless prisms, m. p. 172° . The *diketo-dicarboxylic acid*, $C_{22}H_{32}O_6$, was obtained from this pyro-acid by boiling in alcoholic solution with sodium ethoxide. The sodium salt crystallises in needles. The free acid crystallises in large, colourless plates, m. p. 173° . *Solanellitic acid* was prepared both by the oxidation of prosolanellitic acid and of the α -ketotricarboxylic acid, $C_{23}H_{34}O_7$, with fuming nitric acid; it crystallises in white rosettes of needles, m. p. $202-203^\circ$ (decomp.), $[\alpha]_D^{25} +35.1^\circ$ in alcohol. *Pyrosolanellitic acid*, $C_{22}H_{32}O_6$, prepared by heating solanellitic acid at 270° in a vacuum, crystallises as whetstone-shaped crystals, m. p. 272° . *Norsolanellitic acid*, $C_{22}H_{32}O_6$, obtained by oxidising the pyro-acid with fuming nitric acid, crystallises in lustrous needles, m. p. $228-229^\circ$ (decomp.), $[\alpha]_D^{25} +9.9^\circ$ in 1% alcohol. This acid is also obtained together with

another acid by oxidising pyrodeoxybilanic acid with fuming nitric acid. S. S. Z.

Sulphite Liquor Lactone. S. V. HINTIKKA (*Pappers-Traväru- och Industritidskrift for Finland*, 1921, No. 10, 150; *Cellulose-chemie*, 1921, 2, 87—88).—The author has repeated Holmberg's experiment (A., 1921, i, 25) using birch and aspen woods, but failed to obtain the crystalline lactone reported by Holmberg. It may be that this compound is characteristic of the sulphite waste liquor from pine wood.

CHEMICAL ABSTRACTS.

Cubebin. IV. Derivatives of Cubebinolide. EFISIO MAMELI (*Gazzetta*, 1921, 51, ii, 353—374; cf. A., 1908, i, 20; 1909, i, 503; 1913, i, 47).—When subjected to oxidation under various conditions, cubebin always yields a greater or less proportion of cubebinolide, together with other products. Thus, the action of light, mercuric acetate, hydrogen peroxide, silver oxide, dichromate and sulphuric acid, permanganate, etc., on cubebin yields cubebinolide; nitric acid and bromine yield respectively dinitro- and dibromo-cubebinolide, the central grouping undergoing no oxidation. Just as was observed with cubebin, cubebinic esters, and cubebinol, the action of the more energetic oxidising agents, such as potassium permanganate, on cubebinolide or its derivatives results in complete combustion of the alicyclic grouping, with formation of piperonylic acid.

These results show that the non-primary alcoholic group is the point most readily attacked in the cubebin molecule. The formation of a γ -lactone, like the property of yielding internal ethers with a pentagonal nucleus when treated with a dehydrating agent, represents one of the fundamental chemical characters of cubebin.

The compound, m. p. 183—184°, obtained by the action of nitric acid on cubebinolide, is found to be a dinitrocubebinolide, $C_{20}H_{16}O_6(NO_2)_2$, and to be identical with the compound erroneously described by Peinemann (A., 1896, i, 494) as dinitrocubebin, $C_{20}H_{18}O_6(NO_2)_2$. The two nitro-groups pass one into each of the two piperonylic nuclei existing in cubebin; oxidation of dinitrocubebinolide by means of potassium permanganate yields nitro-

piperonylic acid, $CH_2<\begin{array}{c} O \\ \diagup \quad \diagdown \\ O \end{array}\begin{array}{c} NO_2 \\ \diagdown \quad \diagup \\ CO_2H \end{array}$, m. p. 172°.

In the formation of the two bromo-derivatives of cubebin described by Weidel (A., 1878, 80) and by Angeli and Mola (A., 1895, i, 24), respectively, two of the six oxygen atoms present in the cubebin molecule are displaced, so that the molecule undergoes transformation more profound than mere bromination, this being due to the dehydrating action of the hydrobromic acid evolved during the reaction. Treatment of cubebin with bromine in acetic acid solution containing finely divided calcium carbonate yields: (1) A compound, m. p. 177—178°, which contains two bromine atoms in the molecule, exhibits no lactonic properties, and is to be investigated later, and (2) the compound, $C_{20}H_{16}O_6Br_2$, m. p.

137°, which was obtained previously by the action of bromine on cubebinolide in alcoholic solution and may be regarded as the dibromo-derivative of cubebinolide or as the lactone of dibromo-hydroxycubebinic acid.

Cubebinolide forms monoclinic crystals, m. p. 63–64° [VIOLA and FERRARI: $a:b:c=0.20367:1:0.19998$; $\beta=109^\circ 4'$]. Concentrated sulphuric acid colours cubebinolide reddish-violet or black and becomes green or greenish-red; if water is added, the acid is completely decolorised, whilst the solid remains dark violet.

Dinitrocubebinolide, $C_{20}H_{16}O_6(NO_2)_2$, crystallises in microscopic, canary-yellow, acicular prisms, m. p. 183–184°, and with concentrated sulphuric acid gives a deep orange-yellow solution which slowly turns yellow and, on dilution with water, gradually becomes decolorised and deposits a straw-yellow precipitate. In chloroform solution it is unaffected by bromine.

With concentrated sulphuric acid, dibromocubebinolide gives a reddish-yellow coloration, which changes immediately to violet-brown and then to dirty green, addition of water causing gradual decolorisation of the solution and deposition of a dirty green precipitate.

The amide of *hydroxycubebinic acid*, $C_{20}H_{21}O_6N$, forms stellate aggregates of white, acicular crystals, m. p. 129–130°, decomposing at 165°, and exhibits chemical behaviour analogous to that of the amide of *dibromohydroxycubebinic acid*, $C_{20}H_{19}O_6NBr_2$, which crystallises in tufts or fan-shaped aggregates of silky, white needles, m. p. 164–167°, and decomposes at 170°; with benzene, it forms an additive compound, $6C_{20}H_{19}O_6NBr_2 + 5C_6H_6$. T. H. P.

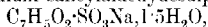
Reactivity of the Nitrobenzaldehydes. GUSTAV HELLER, HILDE LAUTH, and ARNOLD BUCHWALDT (*Ber.*, 1922, **55**, [B], 483–489).—*o*-Nitrobenzaldehyde condenses readily with pyruvic acid in the presence of hydrogen chloride to give *o*-nitrocinnamoyl-formic acid, but similar compounds cannot be obtained from *m*- and *p*-nitrobenzaldehyde. A review of the literature does not indicate any great difference between the reactivities of the three compounds, and this view is confirmed by a series of experiments now recorded. The peculiar action of the *o*-nitroaldehyde towards pyruvic acid is attributed to the intimate relationship of the nitro-group to the ortho-side chain which cannot be easily expressed by a formula.

The action of sodium hydroxide on a solution of *p*-nitrobenzaldehyde and propaldehyde in alcohol gives *p*-nitro- α -methylcinnamaldehyde, pale yellow needles, m. p. 112–113°; the corresponding *m*-nitro-compound has m. p. 83°. *o*-Nitrostyryl dichloromethyl ketone (from *o*-nitrobenzaldehyde and $\alpha\alpha$ -dichloroacetone) crystallises in colourless prisms, m. p. 106–107°; the corresponding *p*- and *m*-nitro-compounds have m. p. 125° and 116–117°, respectively. Ethyl α -*p*-nitrobenzylidenacetate (from an alcoholic solution of the components in the presence of piperidine) forms colourless needles, m. p. 164°, whereas the corresponding ortho-derivative could not be caused to crystallise. *o*-Nitro- α -methyl-

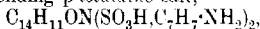
styryl methyl ketone, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CMe} : \text{COMe}$, clusters of pale yellow needles, m. p. $62-63^\circ$, is obtained from *o*-nitrobenzaldehyde and methyl ethyl ketone. It is reduced by zinc dust and concentrated hydrochloric acid in ice-cold alcoholic solution to *o*-amino- α -methylstyryl methyl ketone, m. p., anhydrous, 124° (decomp.), hydrated, m. p. 82° (benzoyl derivative, long needles, m. p. 86°); if reduction is effected without cooling, 2:3-dimethylquinoline, m. p. 68° , is produced. It is remarkable that ring closure of the isolated amino-compound cannot be effected by warming with water or acids. *o*-Nitro- α -methylstyryl methyl ketone, slender, pale yellow needles, m. p. $95-96^\circ$ (corresponding amino-compound, pale yellow prisms, m. p. 120°), and *m*-nitro- α -methylstyryl methyl ketone, m. p. 78° , are also described. H. W.

Preparation of Phenylacetaldehyde. SHINTARÔ KODAMA (Jap. Pat. 37212).—One part of phenylalanine is dissolved in excess of 10–25% sulphuric acid and about 0.5 part of 25–30% sodium nitrite is gradually added at the ordinary temperature; part of the α -hydroxy- β -phenylpropionic acid formed crystallises, the remainder being separated in 90% yield as the calcium salt by boiling with calcium carbonate and adding calcium chloride solution. When heated at $120-140^\circ$ for two to three hours, α -hydroxy- β -phenylpropionic acid is converted into its anhydride, and in a vacuum at $250-300^\circ$ it produces phenylacetaldehyde in 60% yield. The latter substance is isolated as the compound with sodium hydrogen sulphite. Cinnamic acid is produced as a by-product in the second treatment. CHEMICAL ABSTRACTS.

Reduction of Substituted Salicylic Acids. HUGO WEIL and KARL BRIMMER (*Ber.*, 1922, 55, [B], 301–305).—Sulphosalicylic acid is reduced by sodium amalgam in the presence of boric acid to sulphosalicylaldehyde in good yield if the latter is protected by a suitable mixture of sulphite and hydrogen sulphite. The aldehyde is precipitated by the addition of aniline, and the compound thus produced is decomposed by steam in alkaline solution, whereby sodium salicylaldehydesulphonate,



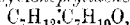
is obtained. Sulphosalicylaldehyde condenses with dimethylaniline in the presence of concentrated sulphuric acid, and the product is converted by sodium hydroxide into the sodium salt, $\text{C}_{22}\text{H}_{20}\text{ON}_2 \cdot \text{SO}_3\text{Na} \cdot 2\text{H}_2\text{O}$, silvery leaflets, which is oxidised to a bluish-green dye. Disulphosalicylic acid is reduced similarly to disulphosalicylaldehyde, the potassium ($+2\text{H}_2\text{O}$) and barium ($+2.5\text{H}_2\text{O}$) salts of which are described. Potassium salicylaldehydedisulphonate is converted by a small amount of *p*-toluidine into the salt, $\text{C}_{14}\text{H}_{11}\text{ON}(\text{SO}_3\text{K})_2 \cdot \text{H}_2\text{O}$, whereas the disulphoaldehyde yields the corresponding *p*-toluidine salt,



with a relatively larger amount of the base. The aldehyde gives a phenylhydrazone which was isolated in the form of its barium salt, $\text{C}_{13}\text{H}_{10}\text{ON}_2(\text{SO}_3)_2\text{Ba}$.

2-Hydroxybenzene-1:3-dialdehyde, long, colourless, hair-like crystals, is obtained by the reduction of *o*-aldehydosalicylic acid; the corresponding *phenylhydrazone*, $C_{20}H_{18}ON_4$, forms yellow crystals. **4-Hydroxybenzene-1:2-dialdehyde**, slender, yellow needles, is prepared similarly from *p*-aldehydosalicylic acid; the corresponding *phenylhydrazone* is a yellow, crystalline precipitate. The aldehyde condenses with dimethylaniline in the presence of concentrated sulphuric acid at 110° to form the substance, $C_{40}H_{38}ON_4$, which is oxidised by lead peroxide to a blue dye. H. W.

Some Derivatives of Suberone. MARCEL GODCHOT and PIERRE BRUN (*Compt. rend.*, 1922, 174, 618—620).—Suberone condenses with itself under the influence of calcium hydride (cf. A., 1919, i, 447) to give *cycloheptylidene**cycloheptanone*,



b. p. $143\text{--}145^\circ/8$ mm.; d_4^{20} 0.9936; n_D^{20} 1.5144. When reduced by sodium in absolute alcohol, this ketone gives *cycloheptylcycloheptanol*, $C_7H_{13} \cdot C_7H_{12}OH$, b. p. $158\text{--}161^\circ/20$ mm.; d_4^{20} 0.9908; n_D^{20} 1.5133, which gives an *allophanic* ester, $C_{14}H_{23}O \cdot CO \cdot NH \cdot CO \cdot NH_2$, m. p. 183° .

When brominated in solution in carbon tetrachloride, suberone yields (?) **2:7-dibromosuberone**, m. p. 68° , which possesses intense sternutatory and blistering properties. With dilute sodium hydroxide in the cold, it gives a *compound*, obtained as a syrup, which is probably a *dihydroxycycloheptanone*. W. G.

Syntheses by means of Sodamide. XI. Substitution Derivatives of Benzoylcyclopropane. ALBIN HALLER and EUGÈNE BENOIST (*Ann. Chim.*, 1922, [ix], 17, 25—37).—Ethyl benzoylacetate condenses with ethylene bromide in the presence of sodium ethoxide to give ethyl 1-benzoylcyclopropane-1-carboxylate (cf. Perkin, T., 1883, 47, 840), giving an *oxime*, m. p. 152° . The ester on saponification gives the free acid, which on heating at 150° is decomposed, giving benzoylcyclopropane. A better yield of this compound is obtained by the action of *cyclopropanecarboxyl chloride* on benzene in the presence of aluminium chloride. Benzoylcyclopropane is decomposed by sodamide in moist benzene, giving cyclopropane and benzamide, but in dry benzene, in the presence of this condensing agent, it reacts with alkyl haloids, giving alkylbenzoylcyclopropanes. In this way, the authors have prepared 1-benzoyl-1-methylcyclopropane, b. p. $127\text{--}128^\circ/18$ mm.; d_4^{20} 1.038; n_D^{20} 1.53659; n_D^{25} 1.54171; giving an *oxime*, m. p. 115° (decomp.), and a *p*-nitrophenylhydrazone, m. p. 112° ; 1-benzoyl-1-allylcyclopropane, b. p. $136\text{--}137^\circ/16$ mm.; and 1-benzoylbenzylcyclopropane, m. p. $33\text{--}5^\circ$; d_4^{25} 1.0795; n_D^{25} 1.57229; n_D^{20} 1.57782; n_D^{25} 1.59231; n_D^{25} 1.90469. With sodamide in moist benzene, these three compounds behave differently. The methyl derivative gives benzamide and methylcyclopropane, the allyl derivative is undecomposed, and the benzyl derivative gives 1-benzylcyclopropane-1-carboxylamide, m. p. 84° , from which the free acid, m. p. 103° , is obtained on hydrolysis. On oxidation, benzoylbenzylcyclopropane gives a *compound*.

$C_{17}H_{14}O_2$, m. p. 86—87°, on which molecular weight determinations do not give results corresponding with dibenzoylcyclopropane.

The following physical constants are recorded: Benzoylcyclopropane, d^{20}_4 1.0453; n^{20}_D 1.53798; n^{20}_B 1.54335; n^{20}_β 1.55701; n^{20}_γ 1.56992; ethyl 1-benzoylcyclopropanecarboxylate, d^{20}_4 1.1355; n^{20}_D 1.52899; n^{20}_B 1.53525; n^{20}_β 1.54862; n^{20}_γ 1.55674. W. G.

The Synthesis of β -Keto-bases from Acetophenone, Formaldehyde, and Amine Salts. C. MANNICH and G. HEILNER (*Ber.*, 1922, 55, [B], 356—365).—The synthesis, previously applied to aliphatic ketones (*A.*, 1917, i, 634) and to cyclohexanone (*A.*, 1920, i, 850), has now been extended to acetophenone as a typical fatty-aromatic ketone.

ω -Dimethylaminopropiophenone hydrochloride, leaflets or needles, m. p. 156°, is readily obtained when equivalent quantities of acetophenone, paraformaldehyde, and dimethylamine hydrochloride are heated to boiling in concentrated alcoholic solution: $\text{COMePh} + \text{CH}_2\text{O} + \text{NHMe}_2 \cdot \text{HCl} \rightarrow \text{COPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2 \cdot \text{HCl} + \text{H}_2\text{O}$. The corresponding base is a colourless liquid, b. p. 110—112°/14 mm. (*oxime*, plates, m. p. 108°). It is oxidised by potassium permanganate to benzoic acid, carbon dioxide, and dimethylamine. It is very readily hydrolysed (by treating the hydrochloride with steam) to dimethylamine and phenyl vinyl ketone. Reduction leads to the formation of different substances according to the experimental conditions. Hydrogenation of the hydrochloride with palladium and hydrogen generally gives α -phenyl- γ -dimethylaminopropene- α -ol hydrochloride, $\text{OH} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2 \cdot \text{HCl}$, leaflets, m. p. 135—136° (the corresponding free base is a liquid; the hydrochloride of the benzoate has m. p. 170°), but, on one occasion, proceeded to the production of γ -dimethylamino-*n*-propylbenzene. Treatment of ω -dimethylaminopropiophenone with activated aluminium in ethereal solution only gives the corresponding secondary alcohol in minor amount, the main product being a mixture of $\alpha\zeta$ -bis-dimethylamino- $\gamma\delta$ -diphenylheptane- $\gamma\delta$ -diols,

$\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CPh}(\text{OH}) \cdot \text{CPh}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2$, [α -form, m. p. 146°, β -variety, m. p. (indefinite) 107°, after softening at about 100°].

The action of methylamine hydrochloride on formaldehyde and acetophenone leads to the production of $\alpha\alpha'$ -bisphenacylmethylmethylamine, $(\text{COPh} \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{NMe}$, and ω -methylaminopropiophenone, $\text{COPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHMe}$. The former, which is formed in larger quantity, crystallises in small rods or needles, m. p. 142°, and yields a hydrochloride, needles grouped in rosettes, m. p. 162°. The latter is a very unstable liquid which is most conveniently obtained by the action of a current of steam on the hydrochloride of the tertiary base: its hydrochloride crystallises in leaflets, m. p. 139—141°. The reduction of $\alpha\alpha'$ -bisphenacylmethylmethylamine by activated aluminium in the presence of moist ether does not proceed uniformly; it was found possible with some difficulty to isolate two crystalline substances [leaflets, m. p. 205°, and slender needles, m. p. (indefinite) 180°, after softening at about 170°] to

which, on the results of analysis, the formula $C_{15}H_{22}O_2N$ is assigned. Probably they represent the racemic and meso-forms of the cyclic pinacone, $NMe \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CPh} \cdot \text{OH} \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CPh} \cdot \text{OH} \end{array}$ H. W.

Glyoximes and Peroxides. D. BIGLAVI (*Gazzetta*, 1921, 51, ii, 324—329).—Angeli, Alessandri, and Aiazzi-Mancini (A., 1911, i, 544) found that the action of magnesium phenyl bromide on the peroxide of piperylmethylglyoxime yields piperonylonitrile and acetophenone, the latter probably resulting from decomposition of a nitronic acid. The author has now extended this reaction to other peroxides and investigated the conditions in which nitriles yield ketones when treated with magnesium alkyl derivatives.

The action of magnesium phenyl bromide on benzonitrile in ethereal solution yields an appreciable proportion of benzophenone, and piperonylonitrile, under similar conditions, gives a compound which melts indistinctly at about 50° , but could not be identified with phenyl piperonyl ketone.

The interaction of magnesium methyl iodide and piperylmethylglyoxime peroxide in benzene solution gives piperonylonitrile and acetopiperone, $CH_3 \cdot O_2 \cdot C_6H_3 \cdot Ac$, the latter being undoubtedly formed by further action of the magnesium derivative on the nitrile. The action of magnesium phenyl bromide on anisylmethylglyoxime peroxide in benzene solution yields anisonitrile and, by treatment of the aqueous liquid with dilute sulphuric acid, a green oil which is probably the nitroso-alcohol derived from the isomeric nitronic acid, $CPhMe \cdot NO \cdot OH \rightarrow NO \cdot CPhMe \cdot OH$; this nitroso-alcohol decomposes rapidly, giving a brown oil, consisting principally of acetophenone.

Closely related to the structure of the peroxides is that of the dioximes obtained when the former are reduced by means of zinc and the calculated proportion of acetic acid. Beckmann and Köster's conclusion that such dioximes are *amphi*-dioximes (A., 1893, i, 474), $\begin{array}{c} R \cdot C \text{---} C \cdot R' \\ | \quad | \\ NOH \quad NOH \end{array}$, is of doubtful accuracy, since in the reaction on which it is based phosphorus pentachloride is used, and preference may be given to the *syn*-dioxime structure corresponding with Koreff's formula for the peroxides, $\begin{array}{c} C \text{---} C \\ | \quad | \\ NO \cdot NO \end{array}$ (A.,

1886, 363). These dioximes exhibit, indeed, properties distinguishing them from their isomerides: they have lower melting points and are unstable, undergoing isomerisation when heated; when their diacetyl derivatives are hydrolysed and, in some cases, when the dioximes themselves are heated, furazans are formed more readily than from the isomeric dioximes.

Extension of Tschugaev's experiments (A., 1908, i, 554) shows that *syn*-glyoximes with both radicles aliphatic form complex nickel compounds, whereas those with one or two aromatic radicles do not form such compounds. Dimethylglyoxime, obtained by reduction of the peroxide, forms the red nickel complex salt. Of the two piperylmethylglyoximes, the γ -compound, m. p. 150° ,

formed on reduction of the peroxide, forms no complex, but the β -dioxime, m. p. 209°, prepared by heating the γ -isomeride at 160°, forms a dark red *nickel complex*, $C_{30}H_{18}O_8N_2Ni$. Of the four dioximes of camphor (Forster, T., 1903, **83**, 519), only the α -isomeride, m. p. 199°, obtained by reduction of the peroxide, forms a *nickel complex*, $C_{30}H_{44}O_8N_2Ni_2$; this result is in agreement with the conclusions given above, since in the camphordioximes the two aliphatic radicles united to the group $\cdot C(NOH) \cdot C(NOH) \cdot$ are joined to form a ring.

Benzoylglyoxime peroxide gives the same dioxime when reduced by means of zinc and the calculated amount of acetic acid as by reduction with platinum black and hydrogen, and the same is the case with camphordioxime peroxide.

T. H. P.

Crystallography of Derivatives of Benzophenone. F. M. JAEGER (*Z. Kryst. Min.*, 1921, **56**, 46—61; from *Chem. Zentr.*, 1921, iii, 1159—1160).—Crystallographic descriptions are given of a number of derivatives of benzophenone. Benzophenone, m. p. 36° and 48·5°; rhombic bipyramidal ($a : b : c = 0.8511 : 1 : 0.6644$). 2-Nitrobenzophenone, m. p. 105°; monoclinic prismatic ($a : b : c = 0.8961 : 1 : 0.4706$, $\beta = 87^\circ 42.5'$). 2-Chlorobenzophenone, lustrous, colourless needles, m. p. 45·5°; monoclinic prismatic ($a : b : c = 0.4985 : 1 : 0.4706$, $\beta = 83^\circ 8'$). 2-Iodobenzophenone, colourless crystals, m. p. 32°; triclinic pinacoidal ($a : b : c = 1.0966 : 1 : 1.4193$, $\alpha = 98^\circ 57'$, $\beta = 83^\circ 22.5'$, $\gamma = 93^\circ 9'$). 2:4-Dibromobenzophenone, colourless plates, m. p. 55°; rhombic bipyramidal ($a : b : c = 0.7168 : 1 : 0.2945$). 2:4'-Dibromobenzophenone, prisms and tablets, m. p. 62°; monoclinic prismatic ($a : b : c = 1.0962 : 1 : 0.5951$, $\beta = 68^\circ 25.5'$). 2-Bromobenzophenone, m. p. 42°; monoclinic prismatic ($a : b : c = 0.5045 : 1 : 0.9322$, $\beta = 83^\circ 24.5'$). 2:4'-Dichlorobenzophenone, m. p. 66°; monoclinic prismatic ($a : b : c = 0.5139 : 1 : 0.4654$, $\beta = 81^\circ 21'$). 2:4:6-Trichlorobenzophenone, m. p. 102°; triclinic pinacoidal ($a : b : c = 1.3908 : 1 : 1.1537$, $\alpha = 120^\circ 41'$, $\beta = 110^\circ 27.5'$, $\gamma = 77^\circ 20'$). 2:4:6-Tribromobenzophenone, m. p. 147°; triclinic pinacoidal ($a : b : c = 1.3939 : 1 : 1.1065$, $\alpha = 120^\circ 59.5'$, $\beta = 108^\circ 44'$, $\gamma = 75^\circ 20'$). 2-Chloro-4'-nitrobenzophenone, yellow tablets from benzene, thick plates or prisms from ethyl acetate, m. p. 107·5°; rhombic bipyramidal ($a : b : c = 2.6857 : 1 : 1.7153$). 2-Chloro-4'-aminobenzophenone, yellow crystals, m. p. 112°; monoclinic prismatic ($a : b : c = 0.5141 : 1 : 0.4824$, $\beta = 81^\circ 5'$). 4-Chloro-3-nitrobenzophenone, short, light yellow prisms, m. p. 105°; rhombic bipyramidal ($a : b : c = 0.9363 : 1 : 0.5740$). 4-Chloro-4'-nitrobenzophenone, light yellow, flat needles, m. p. 100·8°; triclinic pinacoidal ($a : b : c = 1.166 : 1 : 0.995$, $\alpha = 119^\circ 27'$, $\beta = 122^\circ 36'$, $\gamma = 89^\circ 40'$). 4-Bromo-3-nitrobenzophenone, light yellow, flat needles or prisms, m. p. 113°; rhombic bipyramidal ($a : b : c = 1.5453 : 1 : 0.3847$). 4-Bromo-3-aminobenzophenone, light yellow tablets, m. p. 85°; monoclinic prismatic ($a : b : c = 1.9883 : 1 : 1.1745$, $\beta = 86^\circ 58'$). 4:4'-Dibromo-3-nitrobenzophenone, yellow needles, m. p. 119·5°; monoclinic sphenoidal (?) ($a : b : c = 2.6352 : 1 : 4.4498$, $\beta = 89^\circ 10.75'$). 4-Bromo-3:4'-dinitrobenzophenone, long, light yellow needles, m. p. 139·5°; rhombic

*n**

bipyramidal ($a:b:c=1.6350:1:1.288$). 4-Methylbenzophenone, monoclinic prismatic ($a:b:c=1.0117:1:0.4118$, $\beta=84^\circ 46'$); a second form is rhombohedral and hemimorphic ($a:c=1:1.2254$). 3:4'-Dimethylbenzophenone, m. p. 82° ; monoclinic prismatic ($a:b:c=1.0409:1:0.4154$, $\beta=88^\circ 15'$). 2:5-Dimethylbenzophenone, m. p. 36° ; rhombic bipyramidal ($a:b:c=0.8371:1:0.4048$). 2:4:6-Trimethylbenzophenone, m. p. 35° ; rhombic bisphenoidic ($a:b:c=0.7682:1:0.2243$). 2-Bromo-4-ethoxybenzophenone, prisms, m. p. 79.5° ; rhombic bipyramidal ($a:b:c=0.6907:1:0.6915$).

G. W. R.

Hydroxynaphthaquinone. IV. New Derivatives of 2:3:8-Tribromo-5-hydroxy-1:4-naphthaquinone.

ALVIN S. WHEELER and T. M. ANDREWS (*J. Amer. Chem. Soc.*, 1921, **43**, 2582—2587; cf. A., 1919, i, 490).—Further evidence is given of the marked reactivity of the bromine atom in position 8 in 2:3:8-tribromo-5-hydroxy-1:4-naphthaquinone. It can be replaced by chlorine or by hydroxyl, phenylamino-, *o*-tolylamino-, *p*-tolylamino-, or *p*-bromophenylamino-groups. If the bromine atom in position 8 is first replaced by a hydroxyl group and the product then reduced by zinc dust in acid solution, a dibromotetrahydroxynaphthalene is obtained, but if zinc dust in alkaline solution is used, a tetrahydroxynaphthalene is obtained. Reduction of the original tribromonaphthaquinone with zinc dust in acid solution gives a tribromotrihydroxynaphthalene. The sodium salt of 2:3:8-tribromo-5-hydroxy-1:4-naphthaquinone gives ethers when boiled with alkyl haloids.

The following new compounds are described:

1:4:5:8-Tetrahydroxynaphthalene, m. p. 224° . 2:3-Dibromo-1:4:5:8-tetrahydroxynaphthalene, $C_{10}H_6Br_2(OH)_4$, m. p. $164-166^\circ$, giving a tetra-acetyl derivative, m. p. $149-150^\circ$. 2:3-Dibromo-8-hydroxy-5-acetoxy-1:4-naphthaquinone, m. p. 197° . 2:3:8-Tribromo-1:4:5-trihydroxynaphthalene, m. p. $106-107^\circ$, giving a triacetyl derivative, m. p. $219-220^\circ$; and with water a compound, m. p. 168° . 2:3-Dibromo-8-hydroxy-5-methoxy-1:4-naphthaquinone, m. p. $209-210^\circ$, and 2:3-dibromo-8-hydroxy-5-ethoxy-1:4-naphthaquinone, m. p. $134-136^\circ$, giving a sodium salt, which dyes silk a champagne colour. 8-Chloro-2:3-dibromo-5-acetoxy-1:4-naphthaquinone, m. p. $159.5-160^\circ$.

By boiling tribromojuglone in alcoholic solution with certain aromatic bases, the following arylamino-derivatives were obtained: 2:3-Dibromo-5-hydroxy-8-anilino-1:4-naphthaquinone, m. p. $234.5-235.5^\circ$; 2:3-dibromo-5-hydroxy-8-*o*-toluidino-1:4-naphthaquinone, m. p. $187.5-189^\circ$; 2:3-dibromo-5-hydroxy-8-*p*-toluidino-1:4-naphthaquinone, m. p. $216-217^\circ$; 2:3-dibromo-5-hydroxy-8-*p*-bromoanilino-1:4-naphthaquinone, m. p. $254-256^\circ$. With *p*-nitro-aniline a compound, m. p. $159.5-160^\circ$, containing a high percentage of bromine was obtained.

W. G.

Production of Hydroxy-derivatives of Anthraquinone. ARTHUR HUGH DAVIES and SCOTTISH DYES, LTD. (Brit. Pat. 174101).—Dihydroxyanthraquinones are obtained by heating in

an autoclave monochloroanthraquinones and solutions of alkali hydroxides in presence of oxidising agents such as chlorates or nitrates. For example, alizarin is obtained by heating a mixture of 78 parts of 2-chloroanthraquinone, 275 parts of sodium hydroxide, 11.3 parts of sodium chlorate, and 850 parts of water for twenty-four hours at 170°. The reaction mixture is diluted with 2000 parts of water, boiled, filtered, and the residue again extracted with boiling sodium hydroxide solution. From the combined filtrates, the alizarin is precipitated by the addition of hydrochloric acid.

G. F. M.

Alizarin-iron Lakes. ARTHUR W. BULL and J. R. ADAMS (*J. Physical Chem.*, 1921, 25, 660—664).—The adsorption isotherm of *N*/10-sodium hydroxide by hydrated ferric oxide has been determined at 22°. The adsorption of sodium alizarin by hydrated ferric oxide suspensions was also determined at the same temperature and the amount of sodium hydroxide set free ascertained; this quantity was found to be small in all cases. The influence of alizarin on the adsorption of sodium hydroxide by ferric hydroxide is also found to be very small. The experimental data indicate that the iron-alizarin lake described by Biltz (A., 1906, ii, 78) is not a true chemical compound ferric alizarate, but an adsorption complex of ferric hydroxide and sodium alizarin.

J. F. S.

Arylaminoanthraquinone Derivatives. A. LÜTTRINGHAUS and L. EIFFLAENDER (U.S. Pat. 1394851).—The preparation is effected by treating an aminoanthraquinone compound containing one or more amino-groups (substituted or unsubstituted) with metal arylamides in the presence of primary amino-compounds such as aniline. For example, 1-amino-4-anilino-2-methylantraquinone is obtained when magnesium shavings are boiled with aniline and sodamide, and the magnesium anilide caused to react with 1-amino-2-methylantraquinone, the product being extracted with acetone and recrystallised from glacial acetic acid. Variations of the process are described by means of which the following may be prepared: 1-amino-4-anilino-2-methylantraquinone (violet-black prisms, m. p. 244°), (?) 1-amino-4-anilinoanthraquinone (m. p. 232°), 1-amino-4-*p*-toluidino-2-methylantraquinone, di-anilinoanthraquinone (dark violet crystals, m. p. 152°). The last-named compound, when oxidised with air in aniline solution at 90° containing some sodium or potassium hydroxide, yields anthraquinonedihydro-*N*-phenylphenazine, m. p. 233°.

Similar reactions may be applied to the aminochloroanthraquinones.

CHEMICAL ABSTRACTS.

A New Class of Coloured Reduction Products of 1-Benzoylanthraquinones or of 2:3-Phthaloylbenzophenones. ALFRED SCHAARSCHMIDT (*Ber.*, 1922, 55, [B], 489; cf. A., 1915, i, 566, 696; 1916, i, 408).—A reply to Scholl (A., 1921, i, 872).

H. W.

Amino- and Anilino-phenanthraquinones. KURT BRASS and ERWIN FERBER (*Ber.*, 1922, 55, [B], 541—556). Vat dyes cannot be prepared by interaction of phenanthraquinone with *p*-diamines

n* 2

in the same way as from α -naphthaquinone (Pummerer and Brass, A., 1911, i, 654; Brass and Papp, A., 1920, i, 398; Brass, A., 1912, i, 1874) or anthraquinone (D.R.-P. 230409, 243489). Instead, valueless, dark coloured products of high melting point are obtained. After attempts to prepare 2-anilinophenanthraquinone, $C_{20}H_{13}O_2N$, a black powder, by interaction of 2-bromophenanthraquinone with aniline, or acetanilide, or derivatives, had failed, this compound was obtained by heating 2-aminophenanthraquinone (best obtained from the nitro-derivative by means of sodium hyposulphite or sodium hydrogen sulphide) with bromobenzene and pyridine at $160-170^\circ$ in presence of copper. From 2-acetylaminophenanthraquinone, $C_{16}H_{11}O_3N$, reddish-violet needles, m. p. 324° (decomp.), ethyl bromide and pyridine at 180° , 2-ethylaminophenanthraquinone, $C_{16}H_{13}O_2N$, crystallising in violet-black nodules, is obtained. 2-Acetyl-amino-9:10-phenanthraquinyl diacetate, $C_{20}H_{17}O_5N$, needles, m. p. 228° , results from the acetylating reduction of 2-aminophenanthraquinone. 2-op-Dinitroanilinophenanthraquinone, $C_{20}H_{11}O_6N_3$, m. p. 280° , from chloro-2:4-dinitrobenzene, is easily converted into 2-op-dinitroanilinodiphenyleneglycollic acid, a brown, amorphous powder [lead salt ($C_{20}H_{12}O_7N_2$) $_2$ Pb]. Similarly, 2-oo-p-trinitroanilinophenanthraquinone, $C_{20}H_{10}O_8N_4$, minute reddish-brown plates, m. p. $304-305^\circ$, furnishes 2-oo-p-trinitroanilinodiphenyleneglycollic acid, $C_{20}H_{12}O_9N_4$ [lead salt ($C_{20}H_{11}O_9N_4$) $_2$ Pb]. 4-Aminophenanthraquinone is best prepared from the nitro-derivative by means of sodium hydrogen sulphide. 2-Bromo-9:10-phenanthraquinyl dibenzoate (D.R.-P. 151981) is best prepared by benzylation of a solution of the 2-bromophenanthraquinone in sodium hyposulphite solution in presence of hydrogen, and does not react with aniline. J. K.

Syntheses by means of Sodamide. X. The *p*-Amino-benzylidene- and *p*-Aminobenzyl-camphors and some of their Derivatives. ALBIN HALLER and PAUL BOUDIN (*Ann. Chim.*, 1922, [ix], 17, 5-25).—Depolymerised *p*-aminobenzaldehyde condenses with *d*-camphor in the presence of sodamide, giving *d*-*p*-aminobenzylidenecamphor, m. p. 133° ; $[\alpha]_D + 745^\circ$ (in alcohol), which gives an acetyl derivative, m. p. 208° ; $[\alpha]_D + 427^\circ$; a hydrochloride, m. p. 184° (decomp.), a hydrobromide, m. p. 208° (decomp.), and a sulphate. When the sulphate is treated with potassium nitrite and sulphuric acid in alcoholic solution, it yields benzylidenecamphor, but in aqueous solution the product is *p*-hydroxybenzylidenecamphor, m. p. 207° . When *p*-aminobenzylidenecamphor is diazotised and the product submitted to the Sandmeyer reaction, *p*-chlorobenzylidenecamphor, m. p. 109° ; $[\alpha]_D + 385^\circ$; *p*-bromobenzylidenecamphor, m. p. 134° , or *p*-cyanobenzylidenecamphor, m. p. 162° , b. p. $251^\circ/16$ mm. (decomp.); $[\alpha]_D + 425^\circ$, are obtained. If the diazonium salt is coupled with β -naphthol, β -hydroxynaphthalene-1-azo-*p*-benzylidenecamphor, m. p. 220° , is the product. *p*-Aminobenzylcamphor, m. p. 82° ; $[\alpha]_D + 214^\circ$, is obtained by reducing the benzylidene compound in alcoholic solution with sodium amalgam. The following compounds derived from it are described. *p*-Acetyl-

aminobenzylcamphor, m. p. 172°; $[\alpha]_D +176^\circ$; *benzylcamphor*, m. p. 52°; *p-hydroxybenzylcamphor*, m. p. 184°; $[\alpha]_D +406^\circ$; *p-chlorobenzylcamphor*, m. p. 73°; $[\alpha]_D 92.9^\circ$; *p-bromobenzylcamphor*, m. p. 90°; $[\alpha]_D +87.9^\circ$; *p-cyanobenzylcamphor*, m. p. 145°; $[\alpha]_D +334.5^\circ$, and β -*hydroxynaphthalene-1-azo-p-benzylcamphor*, m. p. 129°.

W. G.

Biogenesis of Oil of Peppermint. R. E. KREMERS (*J. Biol. Chem.*, 1922, 50, 31—34).—An investigation of the cohobated oils of American and Japanese peppermints showed that the latter consisted almost wholly of pulgone, whilst the former contained menthone and menthol as main constituents, and, in addition, 1-methylcyclohexan-3-one. Acetone was present in the cohobated aqueous distillate.

Schemes for the possible biogenesis of the main constituents of the oils of peppermint (*Mentha piperita*) and spearmint (*Mentha spicata*) are outlined.

E. S.

Oil of *Satureja montana* of Italian Origin. P. LEONE and E. ANGELESCU (*Gazzetta*, 1921, 51, ii, 386—390).—This oil contains 28% of carvacrol, 1.58% of esters, 10% of alcohols which have not been identified, 27% of cymene, and 14% of dipentene (cf. *J. Soc. Chem. Ind.*, 1922, 269A).

T. H. P.

Oil of *Thymus vulgaris* of Italian Origin. P. LEONE and E. ANGELESCU (*Gazzetta*, 1921, 51, ii, 391—395).—This oil contains 38% of phenols consisting almost solely of thymol, 19% of free alcohols probably composed mostly of borneol and linalool, 18% of cymene, and small proportions of esters and free acids (cf. *J. Soc. Chem. Ind.*, 1922, 269A).

T. H. P.

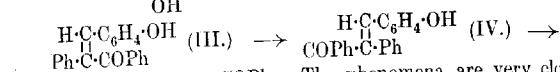
The Composition of the Essential Oil of Turpentine from Aleppo. GEORGES DUPONT (*Compt. rend.*, 1922, 174, 395—398).—The essential oil of turpentine from Aleppo contains a small amount of material which does not distil over except at a temperature much higher than the boiling point of pinene. This fraction is found to consist of *i*-bornyl acetate and a sesquiterpene not identified, the composition of the fresh essence being approximately *d*-pinene 95%, *i*-bornyl acetate 1.14%, sesquiterpene 3.8%.

W. G.

Estimation of the Molecular Magnitude of Caoutchouc by Chemical Methods. C. HARRIES and FRITZ EVERS (*Wiss. Veröffentl. Siemens-Konzern*, 1921, 1, 87—95).—Reduction of the dihydrochloride of caoutchouc in ethylene dichloride solution by means of zinc dust, yields a large amount of α -hydrocaoutchouc as a light yellow, amorphous, somewhat elastic mass melting between 120° and 130°. From its molecular weight in bromoform, it appears to be a polymericide of $C_{35}H_{62}$ or $C_{40}H_{70}$. α -Hydrocaoutchouc is readily converted into an ozonide and yields a hydrochloride (m. p. 190—195°) and a bromide. The conclusion is drawn that the caoutchouc molecule contains 35 or 40 carbon atoms, most probably the latter, and that the structural formula contains eight $CH_2-C(CH_3)-CH-CH_2$ groups joined together in a 32-atom ring.

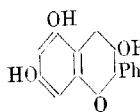
A. R. P.

Ring Opening in the Benzopyrylium Series. HERMAN DECKER and PAUL BECKER (*Ber.*, 1922, 55, [B], 375—394; cf. Decker and Fellenberg, A., 1907, i, 950; 1909, i, 116; Decker and Felser, A., 1908, i, 906, 1003).—The interest in the benzopyrylium dyes has been enhanced greatly by the discovery of the wide distribution in plants. Examination has now been made of the opening of the ring of a pyranol which does not contain a hydroxyl group. A suitable initial material is found in the product of the condensation of deoxybenzoin with salicylaldehyde. The changes which have been realised are expressed by the following scheme:
$$\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}=\text{CPh} \\ | \\ \text{O}=\text{CPh} \end{array} \text{ (I.)} \rightarrow \text{C}_6\text{H}_4 \begin{array}{c} \text{CH}=\text{CPh} \\ | \\ \text{O}---\text{CPh-OH} \end{array} \text{ (II.)} \rightarrow$$



$\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO} + \text{CH}_2\text{Ph} \cdot \text{COPh}$. The phenomena are very closely similar to those observed when coumarin is treated with solutions of alkali hydroxides.

The relationships of the pyranols to the anthocyanidanoles is also discussed. The parent substance of the latter appears to be



3:5:7-trihydroxy-2-phenylbenzopyran (annexed formula) which may be expected to pass by fission of the ring into the derivative of vinyl alcohol, $\text{C}_6\text{H}_2(\text{OH})_3 \cdot \text{CH} \cdot \text{C}(\text{OH}) \cdot \text{COPh}$, and subsequently into the ketone, $\text{C}_6\text{H}_2(\text{OH})_3 \cdot \text{CH} \cdot \text{CO} \cdot \text{COPh}$. The latter would decompose into benzoic and formic

acids, which have been observed frequently, and methylphloroglucinol, which has not been isolated up to the present.

Deoxybenzoin condenses with salicylaldehyde in hydrochloric acid solution to give 2:3-diphenylbenzopyrylium chloride in 88.5% yield (cf. Decker and Fellenberg, *loc. cit.*); if the condensation is arrested by the addition of carbon dioxide or acetic acid when the mixture has attained its maximal colour, *o*-coumarophenone is precipitated in quantitative yield. 2:3-Diphenylbenzopyran-2-ol (formula II), almost colourless plates, m. p. 123—124°, is obtained by the gradual addition of a solution of the double salt of ferric chloride and 2:3-diphenylbenzopyrylium chloride in glacial acetic acid to water; it is almost unaffected by cold, dilute hydrochloric acid or sodium hydroxide solution, but dissolves readily in the hot reagents. It reacts readily with hot aliphatic alcohols, yielding the corresponding ethers, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}:\text{CPh} \\ | \\ \text{O}---\text{CPh-OAlk} \end{array}$ (ethyl ether, m. p.

77—78°; methyl ether, m. p. 75—76°; propyl ether, coarse prisms, m. p. 70—71°; isobutyl ether, prisms, m. p. 68—69°. The ethyl is converted into the isobutyl compound when warmed with an excess of isobutyl alcohol). If the crystalline carbinol is warmed with sodium hydroxide solution (1%) until the maximal intensity of colour is developed and the solution is then cooled, *trans-α-phenyl-o-coumarophenone* [*α*-salicylylidenedeoxybenzoin] (formula IV) is deposited in the form of the characteristic sodium salt, dar-

red, lustrous needles ($+3\text{H}_2\text{O}$), from which the free substance, pale red needles, m. p. $154-155^\circ$, is liberated by carbon dioxide. The latter is re-converted by hydrochloric acid into 2:3-diphenylbenzopyrylium chloride, which is identified as the additive compound with ferric chloride. α -Phenyl-o-coumarophenone is isomerised when heated at its melting point or in the presence of boiling toluene to phenylbenzopyranol, m. p. $123-124^\circ$. It is hydrolysed by boiling alcoholic sodium hydroxide solution to deoxybenzoin and salicylaldehyde. It is converted by methyl sulphate in the presence of sodium hydroxide into the corresponding ether, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CPhBz}$, pale yellow, lustrous needles, m. p. 141° .

The analogy of phenylbenzopyranol with coumarin suggests that, under the action of alkali hydroxide, the sodium salt of an unstable *cis*-phenyl-o-coumarophenone is initially formed which passes into the more stable *trans*-variety. This appears to be the case, since an emulsion of the carbinol is dissolved immediately by sodium hydroxide with the formation of a yellow solution from which concentrated sodium hydroxide precipitates an amorphous yellow salt. Attempts to isolate the free *cis*-phenyl-o-coumarophenone (formula III) were unsuccessful owing to its immediate re-conversion into phenylbenzopyranol. Its intermediate existence is, however, placed beyond doubt by the isolation of its methyl ether, irregular hexagonal platelets, m. p. $111-112^\circ$.

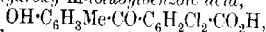
The action of sodium hydroxide on an alcoholic solution of deoxybenzoin and salicylaldehyde leads to the formation of a polymeride of the latter, colourless leaflets, m. p. $120-121^\circ$, in place of the desired diphenylcoumaroketone.

It appeared desirable to follow the sequence of changes with a benzopyrylium salt which leads to the production of a ketone of established constitution. This is effected with 2-phenylbenzopyranol. The colourless emulsion of the latter is slowly dissolved by sodium hydroxide, probably with initial formation of the *cis*-ketone; when, however, the solution has attained its maximal intensity of colour, it yields *trans*-coumarophenone when treated with carbon dioxide or the sodium salt of this compound when treated with concentrated sodium hydroxide. Protracted warming of the alkaline solution of *trans*-coumarophenone leads to the almost quantitative production of acetophenone and salicylaldehyde.

H. W.

The Xanthone Series. ANNA MARIE V. DEM KNESEBECK and FRITZ ULLMANN (*Ber.*, 1922, **55**, [B], 306-316).—A continuation of the work of Ullmann and Schmidt (*A.*, 1920 i, 53).

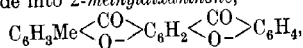
3:6-Dichlorophthalic anhydride condenses with *p*-cresol in the presence of aluminium chloride and acetylene tetrachloride to form 3:6-dichloro-2-*p*-hydroxy-*m*-toluylbenzoic acid,



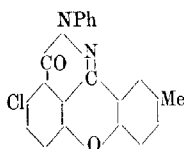
pale brown needles, m. p. 187° . The latter is transformed by boiling potassium carbonate solution (20%) into 7-chloro-2-

methylxanthone-8-carboxylic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_2\text{Cl}\cdot\text{C}_6\text{H}_3\text{Me}$,

pale yellow needles, m. p. 286° (corr., decomp.), the *potassium* salt of which is described. When heated above its melting point, the acid loses carbon dioxide and gives 7-chloro-2-methylxanthone, colourless needles, m. p. 169° (corr.). The acid contains a mobile halogen atom, and is therefore converted by potassium phenoxide in the presence of copper powder into 7-phenoxy-2-methylxanthone-8-carboxylic acid, colourless needles, m. p. 270—280° (corr.), according to the rate of heating (the *sodium* salt is described). The phenoxy-acid is transformed by concentrated sulphuric acid or, preferably, by successive treatment with phosphorus pentachloride and aluminium chloride into 2-methyldioxanthone,



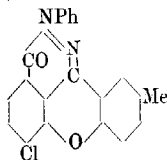
pale yellow needles, m. p. 349—352° (decomp.), which is converted by hydrazine hydrate into the corresponding *azine*, $\text{C}_{21}\text{H}_{12}\text{O}_2\text{N}_2$, long, vivid yellow, matted needles, m. p. 273° (decomp.), which gives a *hydrochloride*, $\text{C}_{21}\text{H}_{13}\text{O}_2\text{N}_2\text{Cl}$, red needles, m. p. about 274° (decomp.). 7-Chloro-2-methylxanthone-8-carboxylic acid yields only traces of methylanilinoxanthonecarboxylic acid when heated with aniline and copper powder, the chief product being 7-anilino-



2-methylxanthone, yellowish-green needles, m. p. 255—259° (corr.). 7-Chloro-N-phenyl-2-methylpyridazonexanthone (annexed formula), yellow needles, m. p. 264—266° (corr.), is readily obtained by heating 7-chloro-2-methylxanthone-8-carboxylic acid with phenylhydrazine; it is converted by boiling aniline in the presence of potassium and

copper acetates into 7-anilino-N-phenyl-2-methylpyridazonexanthone, unusually slender, yellowish-green crystals, m. p. 257—258° (corr.).

3:4-Dichloro-2-p-hydroxy-m-toluybenzoic acid, m. p. 265° (corr.), is prepared from 3:4-dichlorophthalic anhydride in the



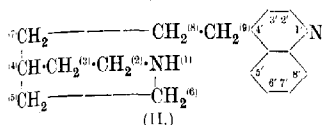
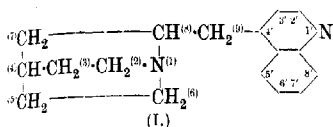
manner described for the 3:6-dichloro-isomeride. It is converted readily by boiling alkalis into 5-chloro-2-methylxanthone-8-carboxylic acid, pale brown needles, m. p. 289—295° (corr.), in which the halogen atom is not replaced by boiling aniline in the presence of copper powder. The acid is transformed by boiling phenylhydrazine into 5-chloro-N-phenyl-2-methylpyridazonexanthone (annexed formula), long, thin needles, m. p. 266—271° (corr.).

H. W.

Some Reactions of Benzanthrone. ARTHUR GEORGE PERKIN and GEORGE DOUGLAS SPENCER (T., 1922, 121, 474—482).

Cinchona Alkaloids. XXIII. Nomenclature and Isomerism Phenomena. PAUL RABE (Ber., 1922, 55, [B], 522—532; d. A., 1921, i, 438).—For the parent substance (I) of the cinchona-alkaloids, the name "*ruban*" is suggested, as a basis of

nomenclature, indicative of their occurrence in the *Rubiaceæ*,



whilst the compound (II) from which the toxins are derived is termed *rubatoxin*. Objection is taken to the extension of the term "quinatoxin" to those 4-quinolyl ketones (Ruzicka, A., 1921, i, 585) not derived from 9-rubatoxanone. Of the thirty-two stereoisomeric derivatives of 3-vinyl-9-rubanol (cinchonine) to be anticipated from the presence of four asymmetric carbon atoms, with an asymmetric trivalent nitrogen atom, only sixteen are actually capable of existence, owing to the fact that the nitrogen atom and one of the carbon atoms constitute the terminals of the quinuclidine bridge. Similarly, only those 9-rubatoxanones in which the configuration of the atoms and groups attached to the nitrogen atom of the piperidine ring is suitable can give rise to 9-rubanones. Probably for this reason, the yield of 9-rubanone from 9-rubatoxanone (see following abstract) is only 50% (a methoxyrubatoxanone gave a similar result), although those rubatoxanones derived from the alkaloids themselves by the Pasteur rearrangement, and therefore having the necessary configuration, under similar conditions furnish yields of at least 80%.

J. K.

Cinchona Alkaloids. XXIV. Synthesis of Vinyl-free Quinatoxins and Quinaketonones. PAUL RABE, KARL KINDLER, and OTTO WAGNER (*Ber.*, 1922, 55, [B], 532—541).—An account of the synthesis, previously foreshadowed (A., 1920, i, 78), of 6'-methoxy-9-rubatoxanone and of 6'-methoxy-9-rubanone. Ethyl β-4-piperidylpropionate, for the preparation of which improvements are described, furnishes a 1-benzoyl derivative, $\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}$, a yellow oil, b. p. $240^\circ/8$ mm., from which, by condensation with ethyl cinchonate and subsequent hydrolysis, 9-rubatoxanone is obtained as a viscid, yellow oil, with a bitter taste, and showing the reactions of the cinchotoxins (*platinichloride*, $\text{C}_{17}\text{H}_{29}\text{ON}_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$). From its 8-bromo-derivative (*dihydrobromide*, yellow crystals, m. p. 184°), 9-rubanone is obtained in 50% yield by the action of sodium carbonate solution; it forms a viscid, yellow oil, with a bitter taste (*picrate*, $\text{C}_{23}\text{H}_{21}\text{O}_8\text{N}_6$, yellow needles, m. p. $170\text{--}180^\circ$). A similar series of compounds follows from the replacement of ethyl cinchonate by ethyl quinate in the above reactions. 6'-Methoxy-9-rubatoxanone (*platinichloride*, $\text{C}_{18}\text{H}_{25}\text{O}_3\text{N}_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$, sinters at 265° and melts at $278\text{--}285^\circ$ after drying in a vacuum; *monopicrochlorate*, $\text{C}_{28}\text{H}_{30}\text{O}_7\text{N}_6$, m. p. 132° ; *monopicroate*, an oil) is a viscid, reddish-yellow oil, with a bitter taste, and exhibits the reactions of the quinatoxins.

6'-Methoxy-9-rubanone, from 8-bromo-6'-methoxy-9-rubatoxanone in 40% yield, is an oil with a bitter taste and showing the reactions of quinone; it gives a *picrate*, $C_{24}H_{23}O_9N_5$, sintering at 168° , m. p. $173-174^\circ$. The *monopicolonate*, $C_{28}H_{28}O_7N_6$, m. p. $148-150^\circ$, the *platinichloride*, $C_{18}H_{20}O_2N_2H_2PtCl_6 \cdot 2H_2O$, needles, m. p. 300° , preceded by sintering at 260° . J. K.

Strychnos Alkaloids. XXX. Reactions of Cacotheline. HERMANN LEUCHS, FRITZ OSTERBURG, and HANS KAEHRN (*Ber.*, 1922, 55, [B], 564-572; cf. A., 1921, i, 883).—The preparation of cacotheline [a name unfortunately given to the nitrate of a base] is described. Like methylcacotheline (A., 1920, i, 178), it contains the quinone grouping, $CO \dots CO$, a nitro-group, secondary and tertiary nitrogen atoms (the latter as nitrate), a carboxylic, and a secondary alcoholic group. *Cacotheline base methyl ester hydrochloride*, $C_{22}H_{24}O_7N_3Cl \cdot H_2O$, forms reddish-brown needles; the *ethyl ester hydrochloride*, $C_{23}H_{26}O_7N_3Cl \cdot 3H_2O$, crystallises in small needles. The *oxime of cacotheline base*, $C_{21}H_{22}O_7N_4 \cdot 4H_2O$, forms yellow needles [*sulphate*, $(C_{21}H_{22}O_7N_4)_2 \cdot H_2SO_4 \cdot rH_2O$, yellow needles; *acetate*, $C_{21}H_{22}O_7N_4 \cdot C_2H_3O_2 \cdot 4H_2O$, yellow needles; *nitrate*, $C_{21}H_{22}O_7N_4 \cdot HNO_3 \cdot H_2O$, prisms; *hydrobromide*, $C_{21}H_{22}O_7N_4 \cdot HBr \cdot 3H_2O$;

methyl ester, $C_{22}H_{24}O_7N_4$, brown needles; *ethyl ester*, gelatinous]. The *oxime hydrochloride*, $C_{21}H_{23}O_7N_4Cl \cdot 3H_2O$, prepared from cacotheline and hydroxylamine hydrochloride, crystallises in yellow needles and yields a *methyl ester*, $C_{22}H_{25}O_7N_4Cl \cdot 4H_2O$, yellow prisms or needles, and a gelatinous *ethyl ester*. The oxime is reconverted by nitric acid into cacotheline, and by reduction into a *diaminophenol* (*trihydrobromide*, $C_{21}H_{27}O_3N_4Br_3$, brown needles or leaflets). The *methyl ester* of a *nitrosoamine*, $C_{23}H_{25}O_6N_5$, green prisms, results from the action of methyl alcoholic ammonia on the methyl ester of the oxime hydrochloride. *Cacotheline base monophenylhydrazone*, $C_{27}H_{27}O_6N_5 \cdot 4H_2O$, brownish-yellow prisms, is prepared from its *hydrochloride*, $C_{27}H_{28}O_6N_5Cl \cdot 3H_2O$, yellow leaflets, which is obtained from the corresponding oxime. *Cacotheline monosemicarbazone*, $C_{22}H_{24}O_7N_6 \cdot HNO_3 \cdot 3H_2O$, yellow needles, is converted by alkali into the *monosemicarbazone* of the free base, $C_{22}H_{24}O_7N_6 \cdot 4H_2O$, yellow needles or prisms. *Cacotheline base methylmethosulphate*, $C_{23}H_{27}O_{11}N_3S$, yellowish-brown leaflets. J. K.

Some Compounds of Piperidine with Haloids. CLIFFORD S. LEONARD (*J. Amer. Chem. Soc.*, 1921, 43, 2618-2626).—A new series of haloid compounds may be prepared from piperidine by reaction with haloids of tervalent arsenic, antimony, and phosphorus and of quadrivalent silicon, tin, and titanium in normal heptane as solvent. These new compounds are considered to be piperidinium compounds and to correspond with Werner's primary compounds. Confirmation of this belief is afforded by the fact that they themselves further unite with metallic salts as does ammonium chloride. * Thus the piperidine-arsenic compound gives a crystalline additive complex with lead iodide and a pale yellowish-

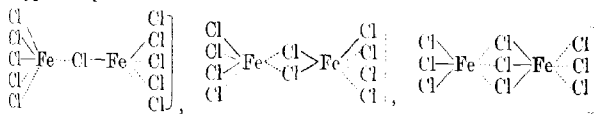
green compound with mercuric iodide. The following compounds are described: *Arsinetri-1-piperidinium chloride*, $\text{As}(\text{C}_5\text{H}_{10}\text{N}, \text{HCl})_3$, crystallising in white needles, m. p. 238° , giving additive compounds with lead iodide, mercuric iodide, and arsenic tri-iodide. *Stibinetri-1-piperidinium chloride*, $\text{Sb}(\text{C}_5\text{H}_{10}\text{N}, \text{HCl})_3$, m. p. 235° . *Silicane-tetra-1-piperidinium chloride*, $\text{Si}(\text{C}_5\text{H}_{10}\text{N}, \text{HCl})_4$, m. p. 238° . *Dichlorostannanedi-1-piperidinium chloride*, $\text{SnCl}_2(\text{C}_5\text{H}_{10}\text{N}, \text{HCl})_2$, m. p. 201° . *Titananetetra-1-piperidinium chloride*, $\text{Ti}(\text{C}_5\text{H}_{10}\text{N}, \text{HCl})_4$, which was very unstable and could not be obtained pure. A phosphorus compound was also prepared, but could not be isolated in a sufficiently pure state for analysis.

These compounds could be hydrolysed with dilute alkali and the free piperidine distilled into standard acid and estimated. This, coupled with the estimation of chlorine in the distillation residues, served as the method of analysis, as carbon could not be estimated by the combustion method.

α -Methylamyl iodide reacts with piperidine in heptane to give α -methylamylpiperidinium iodide, $\text{C}_5\text{H}_{13}\cdot\text{C}_5\text{H}_{10}\text{N}, \text{HI}$, m. p. 133° . This is considered to be analogous in structure to the piperidine-metalloid compounds described above.

W. G.

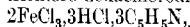
The Constitution of some Ferri-chloride(-thiocyanate, -nitrate) Compounds with Pyridine or Quinoline. R. F. WEINLAND and A. KISSLING (*Z. anorg. Chem.*, 1921, **120**, 209—231).—A large number of new complex compounds containing ferrie chloride and pyridine or quinoline, with or without other constituents, have been prepared and formulæ suggested for them. It is pointed out that the constitution of such compounds is much more difficult to decide than that of similar cobalt and chromium compounds on account of the greater mobility of the constituents and the necessity for working in non-aqueous solutions. To account for the composition of the majority of the compounds under consideration, it is necessary to assume a complex anion containing two atoms of metal, each having the co-ordination number 6. Assuming that one, two, or three chlorine atoms may form a bridge between the two atoms of iron, complex anions of the following types are possible:



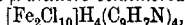
The chlorine atoms can be replaced by other groups in the usual way. The following compounds are described.

(1) *Pyridinium tetrachloroferrate*, $[\text{FeCl}_4]\text{HC}_5\text{H}_5\text{N}$, crystallises from a concentrated hydrochloric acid solution of its constituents in bright yellow needles, stable in dry air.

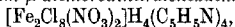
(2) *Tripyridinium- μ -trichloro-hexachlorodiferrate*,



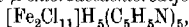
is not new, and is the most readily prepared of these compounds. The formula suggested is $[\text{Cl}_3\text{Fe}:\text{Cl}_3\text{Fe}:\text{Cl}_3]\text{H}_3(\text{C}_5\text{H}_5\text{N})_3$.

(3) *Tetraquinolinium-μ-dichloro-octachlorodiferrate*,

forms olive-green crystals of rhombohedral habit from alcoholic or aqueous hydrochloric acid solution.

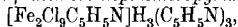
(4) *Tetrapyridinium-μ-dichlorodinitratohexachlorodiferrate*,

crystallises from an aqueous solution of ferric nitrate and pyridine hydrochloride in yellow needles. The corresponding quinoline salt is similar, and both are stable in dry air.

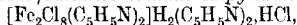
(5) *Pentapyridinium-μ-chlorodecachlorodiferrate*,

was obtained in the form of green leaflets from an alcoholic solution of (2) and pyridine hydrochloride in the mol. ratio 1 : 10 to 1 : 20. It is very hygroscopic and unstable.

(6) *Tripyridinium-hexachloroferrate*, $(\text{FeCl}_6)[\text{H}_3(\text{C}_5\text{H}_5\text{N})_3]$, is obtained instead of (5) when a greater proportion of pyridine hydrochloride is used, and forms unstable pale green leaflets.

(7) *Tripyridinium-μ-dichloro-heptachloropyridinediferrate*,

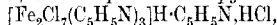
is obtained by triturating (2) with 1 mol. proportion of pyridine in ether; it forms an orange, crystalline powder. The orange colour is characteristic of compounds containing pyridine in the complex anion.

(8) *Dipyridinium-μ-dichloro-hexachlorodipyridinediferrate*,

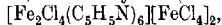
can be obtained from (7) by crystallisation from alcohol, together with (10), and is closely related constitutionally to (11); it forms square, orange leaflets.

(9) *Dipyridinium-μ-dichloro-tetrachlorodinitratodipyridinediferrate*,

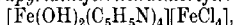
$[\text{Fe}_2\text{Cl}_6(\text{NO}_3)_2(\text{C}_5\text{H}_5\text{N})_2]\text{H}_2(\text{C}_5\text{H}_5\text{N})_2$, from an alcoholic solution of ferric chloride, pyridine, and lithium nitrate; brown aggregates of needles and prisms. By recrystallisation from alcohol, it reverts to (8).

(10) *Pyridinium-μ-dichloro-pentachlorotripyridinediferrate*,

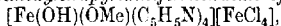
is obtained in orange crusts from an alcoholic solution of (8) with pyridine.

(11) *Hexapyridine-μ-dichlorodiferriditetrachloroferrate*

is obtained from a dry alcoholic solution of (2) with pyridine. It forms irregular, six-sided leaflets or tablets, deep brown in colour, and when freshly prepared can be recrystallised unchanged from alcohol, ethyl acetate, or acetone. Its probable constitution is discussed at length and the conclusion is that it probably contains a complex kation containing pyridine combined with two $[\text{FeCl}_4]$ anions.

(12) *Dihydroxytetrapyridineferritetetrachloroferrate*,

garnet-red, thick crystals from an alcoholic solution of ferric chloride (1 mol.) and pyridine (10 mols.).

(13) *Hydroxymethoxytetrapyridineferritetetrachloroferrate*,

forms a heavy, yellow, crystalline powder when (11) is crystallised

from methyl alcohol, or it can be prepared from its constituents in methyl alcohol.

(14) *Hydroxymethoxytetrapyridineferritetrahiocyanatoferrate* is constituted analogously to (13). It forms a heavy, reddish-black, crystalline powder.

(15) *Octapyridine- μ -dichlorodiferrichloride*, $[\text{Fe}_2\text{Cl}_2(\text{C}_5\text{H}_5\text{N})_8]\text{Cl}_4$, obtained from a solution of anhydrous ferric chloride in pyridine, forms deep red crystals, decomposed by alcohol.

The electrical conductivities of some of the compounds in alcohol were determined and confirmed, in the case of those compounds stable in alcohol, the constitutions given above. E. H. R.

Preparation of Hydrogenated N-Alkylpyridine-3-carboxylates. RICHARD WOLFFENSTEIN (D.R.-P. 340873; from *Chem. Zentr.*, 1921, iv, 1102).—N-Alkylhaloids of alkylpyridine-3-carboxylates are treated with metals and hydrogen haloids in the presence of non-hydrolysing solvents. For example, methyl pyridine-3-carboxylate-N-methochloride is dissolved in methyl alcohol. Tin is added and a current of hydrogen chloride is passed for three to four hours at 100° , whereby *methyl 1-methylhexahydro-pyridine-3-carboxylate* is formed as a liquid, b. p. $86-89^\circ/21.5$ mm. The 1-methochloride of methyl pyridine-3-carboxylate can also be reduced without warming by tin and hydrogen chloride, using formic acid as a solvent. *Ethyl pyridine-3-carboxylate-N-ethiodide* dissolved in alcohol may be similarly reduced by magnesium and hydrogen chloride. The products have therapeutic uses.

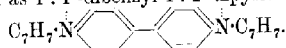
G. W. R.

Preparation of N-Alkylhaloids of Methyl Pyridine-3-carboxylate [Methyl Nicotinate]. RICHARD WOLFFENSTEIN (D.R.-P. 340874; from *Chem. Zentr.*, 1921, iv, 1102).—Methyl pyridine-3-carboxylate is treated with alkyl haloids. For example, methyl pyridine-3-carboxylate is heated at 100° under pressure with methyl bromide and methyl alcohol for forty-eight hours. After removal of methyl alcohol by distillation, the *N-methobromide* is obtained from the residue; it forms crystals, m. p. 71° . The *N-methiodide* forms light yellow crystals, m. p. 130° . The *N-methochloride* forms white crystals, m. p. 98° . The compounds have therapeutic uses.

G. W. R.

Free Ammonium Radicles. III. Existence of N-Benzylpyridinium. ERNST WEITZ and RICHARD LUDWIG (*Ber.*, 1922, 55, [B], 395-413).—In a previous communication (A., 1921, i, 894), Weitz, Nelken, and Ludwig have described the isolation of a red, crystalline substance which gives deep blue solutions in methyl and ethyl alcohols from 1:1'-dibenzyltetrahydro-4:4'-dipyridyl (cf. Hofmann, A., 1881, 921; Emmert, A., 1919, i, 455; 1920, i, 331), which they considered to be 1-benzylpyridinium. This conception has been found to require modification, since the product formed by the iodination of the blue solution, $\text{C}_{24}\text{H}_{22}\text{N}_2\text{I}_2$, short, red needles, m. p. 232° , has been converted into a sparingly soluble *perchlorate*, slender needles, m. p. 257° , which is not identical

with 1-benzylpyridinium perchlorate, as the melting points of the compounds differ by about 160°. Also, it has now been found possible to prepare the crystalline iodide (see above) by titration of solutions of the radicle, preferably in acetone or chloroform, with iodine; the compound contains the halogen in completely ionisable form, but is distinguished from 1-benzylpyridinium iodide by its much smaller solubility in water. Each pyridine nucleus requires approximately one atom of iodine. Formation of the deep blue, oxidisable solution from the iodide is effected readily by zinc dust (preferably in the presence of alcohol or glacial acetic acid); under these conditions, 1-benzylpyridinium chloride is known to remain unchanged. The phenomena are thus closely analogous to those observed with benzoylpyridinium (Weitz, Roth, and Nelken, A., 1921, i, 804), and the probability thus suggested that the radicle is a dipyridyl compound is confirmed by its production from 1:1'-dibenzyl-4:4'-dipyridinium dichloride and zinc dust; on the assumption, therefore, that the substance is a radicle, it must be regarded as 1:1'-dibenzyl-4:4'-dipyridinium,



(An alternative quinoid formula, $\text{C}_7\text{H}_7\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} = \begin{array}{c} \diagdown \quad \diagup \\ \diagup \quad \diagdown \end{array} \text{N}\cdot\text{C}_7\text{H}_7$, is

discussed which, although appearing rather less probable, cannot be discarded completely.) The new conception explains the necessity of the presence of oxygen for the production of the radicle from Hofmann's dibenzyltetrahydridipyridyl. The ready removal of two atoms of hydrogen from the latter appears nearly as difficult to explain as is its oxidation by silver nitrate to the unimolecular pyridinium salt as recorded by Hofmann; this observation is confirmed, but, on the other hand, it is shown that the new radicle gives exclusively a dibenzylidipyridinium salt when treated with silver nitrate. In addition, it is found that the freshly-prepared solution of Hofmann's product is only moderately oxidisable and that only such solutions as have been heated in the absence of air are brownish-yellow and successively become immediately deep blue and ultimately colourless when treated gradually with air. Similarly, a cold, freshly-prepared solution of Hofmann's compound immediately decolorises iodine in the absence of air, a pale green coloration being developed which is discharged by further addition of the halogen; that portion of the product of the reaction which is soluble in water consists almost entirely of unimolecular *N*-benzylpyridinium iodide which contains only the merest trace of dipyridyl derivative. When, on the other hand, a solution of iodine is added gradually to a boiling solution of Hofmann's compound in the absence of air, a deep blue colour is developed which disappears on further addition of the halogen. The reaction is not smooth or quantitative. The product of the change, which is soluble in water, contains the iodides of dibenzylidipyridinium and of benzylpyridinium. The former is never produced except from solutions which* have become blue, and therefore owes its origin to the formation of the radicle under the influence of halogen.

Since the formation of the di-iodide is invariably accompanied by that of the mono-iodide, it is clear that the original Hofmann's compound is converted only gradually in hot solution into the parent substance of the bimolecular radicle; the constitution of the latter and of Hofmann's compound is not yet definitely elucidated.

The authors' experience with benzylpyridinium indicates that, in spite of the results of determinations of the molecular weight, benzylpyridinium (A., 1921, i, 804) is really a bimolecular product, particularly in view of its ready convertibility into 4:4'-dipyridyl.

1:1'-Diacetyltetrahydro-4:4'-dipyridyl (cf. Dimroth and Heene, this vol., i, 48) appears to resemble the benzyl derivative in requiring oxygen for the development of the blue colour in its solutions.

H. W.

Condensation of Acetophenone. III. C. GASTALDI (*Gazzetta*, 1921, 51, ii, 289—306; cf. A., 1916, i, 31).—The hydrocarbon, $(C_{25}H_{22})$, obtained by condensation of acetophenone under the agency of potassium hydroxide (A., 1900, i, 603; 1901, i, 604; 1904, i, 32) reacts with benzoyl chloride in presence of aluminium chloride, yielding 2:4:6-triphenylpyrylium chloride, $CPh \begin{smallmatrix} \text{CH} \cdot CPh \\ \text{CH} \cdot CPh \end{smallmatrix} \gg O \cdot Cl$.

Similar pyrylium derivatives are obtained also in the same way from the homologous hydrocarbon, $C_{28}H_{28}$, obtained from *p*-tolyl methyl ketone, and from the interaction of either of these hydrocarbons with other acid chlorides; certain of the latter, however, fail to react in this way, and in no case is the reaction quantitative. Sublimed aluminium chloride, but not ferric chloride or zinc chloride, serves as condensing agent. As diluent, carbon disulphide gives the best results and nitrobenzene may be used, but light petroleum cannot be employed. The results obtained are explainable according to Delacré's suggestion that the hydrocarbon $C_{25}H_{22}$ is 1:3:5-triphenyl- $\Delta^{1,3}$ -cycloheptadiene (A., 1920, i, 165, 236).

The hydrocarbon, $C_{28}H_{28}$, crystallises in colourless cubes, m. p. 122° , and dissolves in concentrated sulphuric acid to a red solution showing green fluorescence.

2:4:6-Triphenylpyrylium chloride gives: (1) with nitric acid, the corresponding *nitrate*, $C_{23}H_{17}O \cdot NO_3$, golden-yellow needles, m. p. 149° (decomp.), (2) with sodium acetate, α -hydroxy- ϵ -keto- γ -c-triphenyl- $\Delta^{\epsilon,\gamma}$ -pentadiene, and (3) with ammonia, 2:4:6-triphenylpyridine.

4:6-Diphenyl-2-*p*-chlorophenylpyrylium chloride, obtained from the hydrocarbon $C_{25}H_{22}$ and *p*-chlorobenzoyl chloride (1) forms the *nitrate*, $CPh \begin{smallmatrix} \text{CH} \cdot C(C_6H_4Cl) \\ \text{CH} \cdot CPh \end{smallmatrix} \gg O \cdot NO_3$, which crystallises in slender, yellow needles, m. p. 161° (decomp.), and dissolves in acetic acid, giving a solution showing green fluorescence and in concentrated sulphuric acid giving a non-fluorescent, orange-yellow solution; (2) when treated with ammonia solution, yields 4:6-diphenyl-2-*p*-chlorophenylpyridine, $N \begin{smallmatrix} \text{C}(C_6H_4Cl) \cdot CH \\ CPh \cdot CH \end{smallmatrix} \gg CPh$, which crystallises

in colourless needles, m. p. 137°, and in concentrated sulphuric acid gives a solution showing blue fluorescence; (3) when treated with sodium acetate, gives the yellow, flocculent pseudo-base, which was not obtained crystalline.

4 : 6-Diphenyl-2-*p*-bromophenylpyridine, $N \left\langle \begin{array}{c} C(C_6H_4Br) \cdot CH \\ CPh = CH \end{array} \right\rangle CPh$,

prepared from 4 : 6-diphenyl-2-*p*-bromophenylpyrylium chloride, forms colourless laminae, m. p. 154–155°, and yields a non-fluorescent solution in concentrated sulphuric acid.

4 : 6-Diphenyl-2-*p*-tolylpyrylium chloride, prepared from the hydrocarbon $C_{15}H_{23}$ and *p*-toluoyl chloride, (1) forms the nitrate,

$CPh \left\langle \begin{array}{c} CH \cdot C(C_6H_4Me) \\ CH = CPh \end{array} \right\rangle O \cdot NO_3$, which crystallises in lustrous, orange-

yellow laminae, m. p. 155° (decomp.), and in acetic acid gives a solution showing green fluorescence and in concentrated sulphuric acid an orange-yellow coloration showing faint green fluorescence; (2) with sodium acetate, gives α -hydroxy- ϵ -keto- $\alpha\gamma$ -diphenyl- ϵ -*p*-tolyl- $\Delta^{\alpha\gamma}$ -pentadiene (cf. Dilthey, A., 1921, i, 188); (3) with ammonia solution yields 4 : 6-diphenyl-2-*p*-tolylpyridine, $C_{24}H_{18}N$, which crystallises in colourless needles, m. p. 111°, and in concentrated sulphuric acid solution shows blue fluorescence.

2-Phenyl-4 : 6-di-*p*-tolylpyrylium chloride, prepared by the interaction of the hydrocarbon $C_{25}H_{28}$ and benzoyl chloride, (1) yields the ferric chloride compound, $FeCl_4 \cdot O \left\langle \begin{array}{c} CPh = CH \\ C(C_6H_4Me) \cdot CH \end{array} \right\rangle C \cdot C_6H_4Me$,

which crystallises in brownish-yellow needles, m. p. 234°; (2) is converted by ammonia solution into 2-phenyl-4 : 6-di-*p*-tolylpyridine, $C_{25}H_{21}N$, which forms colourless laminae, m. p. 138°, and in concentrated sulphuric acid solution exhibits blue fluorescence; (3) is converted by sodium acetate into the pseudo-base, which separates in pale yellow flocks, but undergoes almost immediate alteration.

2-*p*-Chlorophenyl-4 : 6-di-*p*-tolylpyrylium chloride, from the hydrocarbon $C_{28}H_{28}$ and *p*-chlorobenzoyl chloride, (1) yields the corresponding nitrate, $C_{25}H_{20}O_4NCl_4$, which crystallises in bundles of prisms, m. p. 190° (decomp.); (2) is converted by ammonia into 2-*p*-chlorophenyl-4 : 6-di-*p*-tolylpyridine, $C_{25}H_{20}NCl$, which forms colourless needles, m. p. 188°.

2 : 4 : 6-Tri-*p*-tolylpyridine, $C_{26}H_{23}N$, crystallises in long, colourless needles, m. p. 177°, and in concentrated sulphuric acid solution shows blue fluorescence.

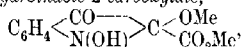
T. H. P.

The Halogenated Isatins. EUGÈNE GRANDMOUGIN (*Compt. rend.*, 1922, 174, 620–623).—The halogenated isatins may be prepared by oxidising the corresponding halogenated indigotins in acetic acid solution by chromic acid. The crude isatin is dissolved in warm dilute alkali to free it from unchanged indigotin and reprecipitated by acid. The following compounds are described: 5 : 7-Dichloroisatin, m. p. 223°, giving an oxime, m. p. 253° (decomp.), and α -phenylhydrazone, m. p. 296–297°. 4 : 7-Dichloroisatin, m. p. 252°, and its oxime, m. p. 245° (decomp.), and

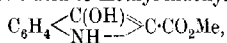
phenylhydrazone, m. p. 265°. 4-Chloro-5-bromoisatin, m. p. 273—274°, its *oxime*, m. p. 253—254° (decomp.), and *phenylhydrazone*, m. p. 278°. 5:7-Dibromoisatin, m. p. 250°, its *oxime*, m. p. 272° (decomp.), and *phenylhydrazone*, m. p. 297—298°. 4:5:6:7-Tribromoisatin, m. p. 257—258°. 4:5:6:7-Tetrachloroisatin, m. p. 294—295°, and its *phenylhydrazone*, m. p. 293°. The oximes and phenylhydrazones are in all cases β -substituted derivatives. The absorption of these compounds in the ultra-violet has been studied and some of the results are given, indicating that the absorption in the ultra-violet of these substituted derivatives is essentially of the same character as that of the parent substance. W. G.

Isatogens. GUSTAV HELLER and WERNER BOESSNECK (*Ber.*, 1922, 55, [B], 474—482).—Treatment of certain highly-coloured isatogens (cf. Pfeiffer, A., 1916, i, 327) with alcoholic hydrogen chloride has led to the formation of less intensely coloured compounds, which, according to Ruggli (A., 1919, i, 221), can only be formulated in Baeyer's original manner, $O \leq \overset{N}{\underset{CR \cdot CO}{\text{C}}} \text{H}_4$. Further investigation, however, has shown that they are additive compounds of the isatogen and the alcohol, $C_6H_4 \leq \overset{CO}{\underset{N(OH)}{C}} \text{C} \leq \overset{OR}{\underset{CO_2R'}{C}}$, and that they are also formed in the complete absence of halogen acid.

Methyl isatogenate is transformed by methyl alcoholic hydrogen chloride (1%) at the atmospheric temperature into *methyl 1-hydroxy-3-keto-2-methoxydihydroindole-2-carboxylate*,



pale, lemon-yellow crystals, m. p. 171° (decomp.), after previous darkening. In the presence of pyridine, it is converted by acetyl chloride into the *acetyl* derivative, almost colourless crystals, m. p. 95—96°, and by benzoyl chloride into the *benzoyl* compound, $C_{18}H_{16}O_6N$, colourless crystals, m. p. 141° (decomp.). It is reduced by zinc dust and acetic acid to methyl indoxylate,



which is obtained more readily from methyl isatogenate. Reduction of the two substances by zinc dust and acetic acid in the presence of methyl alcohol gives a *polymeride* of methyl indoxylate of unknown molecular weight, prisms, m. p. about 245° (decomp.) after darkening at 225°. The 1-hydroxy-ester is converted by hydroxylamine hydrochloride into the oxime of methyl isatogenate, m. p. 221°, from which the corresponding *acid*, $C_8H_6O_4N_2$, pale yellow crystals, m. p. 187° (decomp.), is obtained by hydrolysis with cold sodium hydroxide solution. The 1-hydroxy-compound is isomerised by sodium hydroxide to *N*-oxalylanthranilic acid, m. p. 199—200° (decomp.): $C_6H_4 \leq \overset{CO}{\underset{N(OH)}{C}} \text{C} \leq \overset{OMe}{\underset{CO_2Me}{C}} \rightarrow CO_2H \cdot C_6H_4 \cdot N(OH) \cdot CH(OMe) \cdot CO_2Me \rightarrow CO_2H \cdot C_6H_4 \cdot N(OH) \cdot \dot{C} \cdot CO_2H \rightarrow CO_2H \cdot C_6H_4 \cdot NH \cdot CO \cdot CO_2H$.

Ethyl isatogenate and ethyl alcoholic hydrogen chloride give *ethyl 1-hydroxy-3-keto-2-ethoxydihydroindole-2-carboxylate*, yellow prisms, m. p. 158—159°, with subsequent evolution of gas, after darkening at 150°; like ethyl isatogenate, it is converted by hydroxylamine hydrochloride into *ethyl isatogenate oxime*, yellowish-brown octahedra, m. p. 187° (decomp.). Ethyl isatogenate and methyl alcohol give *ethyl 1-hydroxy-3-keto-2-methoxydihydroindole-2-carboxylate*, pale yellow crystals, m. p. 142—143°, whereas methyl isatogenate and ethyl alcohol yield *methyl 1-hydroxy-3-keto-2-ethoxydihydroindole-2-carboxylate*, lemon-yellow crystals, m. p. 176°, with subsequent evolution of gas. Either compound is isomerised by sodium hydroxide to *N-oxalylanthranilic acid*. H. W.

Equilibrium in the System: Lithium Chloride-Quinoline.

JAMES H. WALTON and CLARENCE R. WISE (*J. Amer. Chem. Soc.*, 1922, **44**, 103—104).—The solubility of lithium chloride in quinoline has been determined from 0° to 96°; measurements were not possible beyond this temperature, for the very long time required for saturation at high temperatures brought about a decomposition of the quinoline. The following solubilities in grams of lithium chloride per 100 grams of solvent are recorded: 0°, 0.1515; 25°, 0.3538; 40°, 0.6175; 45°, 1.0328; 50°, 1.1107; 56.4°, 1.1734; 67°, 1.2353; 75°, 0.8180; and 96°, 0.4588. The solid phase in equilibrium with the solution is $2C_9H_7N, LiCl$. This compound is very stable at all temperatures within the range measured. There is evidence of the formation of a second solid phase above 100°, but this was not investigated because of the decomposition of the quinoline. The solubility curve of lithium chloride is shaped like an irregular inverted U with the maximum at 67°. J. F. S.

The Three Aminotriphenylamines. JEAN PICCARD and RAY Q. BREWSTER (*J. Amer. Chem. Soc.*, 1921, **43**, 2630—2631).—*o*- and *m*-Nitrotriphenylamines (cf. Piccard and Larsen, A., 1917, i, 644) were reduced by adding them gradually in acetic acid solution to a mixture of zinc and alcohol. *o*-Aminotriphenylamine, m. p. 145°, gives an *acetyl* derivative, m. p. 130°. *m*-Aminotriphenylamine, m. p. 116°, gives a *hydrochloride* and an *acetyl* derivative, m. p. 167°.

Attempts to reduce the nitrotriphenylamines to their corresponding aminophenols by the electrolytic method were not successful. W. G.

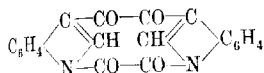
Tetra-substituted Carbamides. T. J. ALBERT, jun. (U.S. Pat. 1393597).—Tetra-substituted carbamides, for example, diphenyldimethylcarbamide are prepared by treating a secondary amine, for example, monomethylaniline, with carbonyl chloride in the presence of an aqueous solution of a basic inorganic compound such as sodium carbonate capable of neutralising the hydrogen chloride which results from the reaction. The reaction is conducted at 95—99° and is complete in two hours. CHEMICAL ABSTRACTS.

Synthesis of Indigotin from Fumaric Acid and Aniline. G. C. BAILEY and R. S. POTTER (*J. Amer. Chem. Soc.*, 1922, **44**, 215—216).—Fumaric acid is brominated in acetic acid solution

and the resulting dibromosuccinic acid is converted into dianilinosuccinic acid (cf. Reissert, A., 1893, i, 565). An equimolecular mixture of potassium and sodium hydroxides is dehydrated in a closed iron pot at 450° with stirring. Sodamide is then added and a stream of dry ammonia passed through the pot, and the sodium salt of dianilinosuccinic acid is slowly added, the mixture being kept at 230–240° for one and a half hours. The fused mass is dissolved in water and air is blown through. The yield of indigotin is 60.4% and its purity is 96.5%. W. G.

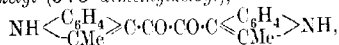
New Syntheses in the Indole Group. VIII. B. ODEO and G. SANNA (*Gazzetta*, 1921, 51, ii, 337–342).—It has been shown (A., 1911, i, 488; 1912, i, 721) that pyrrole, in the form of its magnesium derivative, reacts readily with chlorides of dibasic acids, giving pyrrole derivatives with a double ketonic function analogous to benzil, benzoylacetophenone, and diphenacyl. The indole and methylketole analogues of benzil have now been obtained.

The action of oxalyl chloride on magnesium indolyl bromide yields: (1) *Bis-1:3-indyl (bis-1:3-di-indoyl)* (annexed formula), which forms almost colourless, prismatic crystals, m. p. 200°; (2) principally 3:3-*indyl (3:3-di-indoyl)*,



$\text{NH} \begin{array}{c} \diagup \text{C}_6\text{H}_5 \diagdown \\ \diagdown \text{CH} \diagup \end{array} \text{C} \text{---} \text{CO} \text{---} \text{CO} \text{---} \text{C} \begin{array}{c} \diagdown \text{C}_6\text{H}_5 \diagup \\ \diagup \text{CH} \diagdown \end{array} \text{NH}$, which forms yellow needles or prismatic plates, contracting at about 200°, m. p. 235° (decomp.), and is resistant to the action of boiling alkali hydroxide solution, but yields indole-3-carboxylic acid when fused with potassium hydroxide; (3) a small proportion of 1:1-*indyl (1:1-di-indoyl)*, $\text{CH} \begin{array}{c} \diagup \text{C}_6\text{H}_5 \diagdown \\ \diagdown \text{CH} \diagup \end{array} \text{N} \text{---} \text{CO} \text{---} \text{CO} \text{---} \text{N} \begin{array}{c} \diagdown \text{C}_6\text{H}_5 \diagup \\ \diagup \text{CH} \diagdown \end{array} \text{CH}$, which crystallises in colourless prisms, m. p. 218–220°, and yields indole when boiled with 10% potassium hydroxide solution.

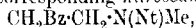
3:3-*Methylketyl (3:3'-dimethylketoyl)*,



prepared by the action of oxalyl chloride on magnesiymethylketole, crystallises in colourless prisms, m. p. 256–257° (decomp.), and gives with phenylhydrazine a condensation product which crystallises in silky, yellow needles, m. p. 192°, and with o-phenylenediamine a condensation product, m. p. (crude) 149°. T. H. P.

Transformations of a Secondary Keto-base. C. MANNICH and G. HEILNER (*Ber.*, 1922, 55, [B], 365–374).—Few secondary keto-bases have been prepared previously and their properties have been little studied. The comparatively ready availability of ω-methylaminopropiophenone (this vol., i, 351) has led the authors to make an extended study of its reactions.

ω-Methylaminopropiophenone hydrochloride is converted by nitrous acid into the corresponding *nitrosoamide*,



large, colourless, prismatic rods or needles, m. p. 66°, which is

reduced by zinc dust and acetic acid in methyl alcoholic solution to 3-phenyl-1-methylpyrazoline, $\text{NMe} \langle \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{N} = \text{CPh} \end{smallmatrix} \rangle$ unctuous leaflets, m. p. 37° (hydrochloride, needles, m. p. 162°), the hydrazine, $\text{CH}_2\text{Bz} \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{NH}_2$, being probably formed intermediately.

ω -Methylaminopropiophenone hydrochloride reacts normally with potassium cyanate, giving as-phenacylmethylmethylcarbamide, $\text{COPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{CO} \cdot \text{NH}_2$, colourless needles, m. p. 123–124°, which is insoluble in cold dilute acids, but readily soluble in solutions of alkali hydroxide, pointing thus to its existence in the enolic form, $\text{OH} \cdot \text{CPh} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{CO} \cdot \text{NH}_2$. It is converted slowly in alkaline solution, more rapidly by regulated treatment with warm dilute acid into 2-keto-4-phenyl-1-methyl-1 : 2 : 5 : 6-tetrahydro-

pyrimidine, $\text{NMe} \langle \begin{smallmatrix} \text{CO} - \text{N} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \rangle \text{CPh}$, m. p. 152–154°, after previous softening. The latter is transformed rapidly by an excess of warm dilute mineral acid into a mixture of equivalent amounts of 2-keto-

4-phenyl-1-methyl-1 : 2-dihydropyrimidine, $\text{NMe} \langle \begin{smallmatrix} \text{CO} - \text{N} \\ \text{CH} : \text{CH} \end{smallmatrix} \rangle \text{CPh}$, matted needles, m. p. 217°, and 2-keto-4-phenyl-1-methylhexahydro-

pyrimidine, $\text{NMe} \langle \begin{smallmatrix} \text{CO} - \text{NH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \rangle \text{CHPh}$, m. p. 115–116°, the phenomenon being thus similar to that observed by Knoevenagel and Fuchs in the case of dihydrolutidinedicarboxylic ester. The relationship of the di- and tetra-hydropyrimidine derivatives to the hexahydro-compound is placed beyond doubt by the observation that the latter is produced when either of the others is treated with hydrogen in the presence of palladised animal charcoal. The hexahydro-compound does not decolorise bromine. On the other hand, 2-keto-4-phenyl-1-methyl-1 : 2-dihydropyrimidine is converted smoothly by bromine in glacial acetic acid solution into 2-keto-4-phenyl-1-methyl-1 : 2-dihydropyrimidine 5 : 6-dibromide, $\text{NMe} \langle \begin{smallmatrix} \text{CO} - \text{N} \\ \text{CHBr} \cdot \text{CHBr} \end{smallmatrix} \rangle \text{CPh}$, pale yellow, lustrous leaflets, m. p. 260°

(decomp.). The tetrahydropyrimidine derivative is transformed by two molecular proportions of bromine in glacial acetic acid solution into a colourless, unstable crystalline substance, decomp.

260°, to which the constitution $\text{NMe} \langle \begin{smallmatrix} \text{CO} - \text{NH} \\ \text{CHBr} \cdot \text{CHBr} \end{smallmatrix} \rangle \text{CBrPh}$ is assigned; it is considered that the initial action of the bromine consists in the conversion of the tetra- to the di-hydro-derivative which then unites with a molecular proportion of hydrogen bromide and bromine with formation of the tribromide. The yellow dibromide readily loses hydrogen bromide under the action of sodium hydrogen carbonate, and passes into 6(15)-bromo-2-keto-4-phenyl-1-methyl-1 : 2-dihydropyrimidine, colourless, slender needles, m. p. 177°. This monobromide is converted by bromine in glacial acetic acid solution into a highly unstable, orange-coloured tetra-bromide, but the reaction appears to be complicated and not entirely due to simple addition of bromine.

As the salt of a secondary base, ω -methylaminopropiophenone hydrochloride is able to condense with formaldehyde and ketones or substances with reactive hydrogen atoms; thus with antipyrine it gives α -phenacylmethyl- α -antipyrino-4-methylmethylaniline.

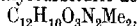
$$\text{CH}_2\text{Bz}\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{C}\begin{smallmatrix} \text{CO}\cdot\text{NPh} \\ \text{CMe}\cdot\text{NMe} \end{smallmatrix}, \text{ thin, slender needles, m. p. } 86^\circ; \text{ the corresponding hydrochloride has m. p. } 164^\circ. \quad \text{H. W.}$$

Some Ketones of the Pyrazole Series. C. A. ROJAHN (*Ber.*, 1922, 55, [B], 291—294).—It has been shown previously that very varying yields of ketones are obtained by the application of the Friedel-Crafts method to 5-chloro-1-phenyl-3-methylpyrazole (Michaelis and Rojahn, A., 1917, i, 480). The influence of substituents in the pyrazole ring on the reactivity of the hydrogen atom in position 4 with respect to the ketone synthesis has been investigated in greater detail, and it is found that only those chloropyrazoles which have an aryl group in position 1 yield ketones, whereas it is not very material whether the substituent in position 3 is an aryl or alkyl group. The synthesis cannot be effected with 5-pyrazolones which yield *O*- or *O*- and *N*-benzoyl derivatives.

The following individual substances are described: 5-Chloro-4-benzoyl-1-*p*-tolyl-3-methylpyrazole, $\text{N}\begin{smallmatrix} \text{N}(\text{C}_6\text{H}_4\text{Me})\cdot\text{C}\cdot\text{Cl} \\ \text{CMe} \end{smallmatrix}\text{---CBz}$ (from 5-chloro-1-*p*-tolyl-3-methylpyrazole, benzoyl chloride, and aluminium chloride in the presence of carbon disulphide), colourless, hexagonal plates, m. p. 70° . 5-Chloro-4-benzoyl-1:3-diphenylpyrazole (from 5-chloro-1:3-diphenylpyrazole, m. p. 56° instead of 49° recorded in the literature), needles, m. p. 127° , b. p. $340\text{--}345^\circ/25 \text{ mm.}$ 5-Benzoyl-1-benzoyl-3-methylpyrazole, $\text{N}\begin{smallmatrix} \text{NBz}\cdot\text{OBz} \\ \text{CMe}\cdot\text{CH} \end{smallmatrix}$ (from 3-methyl-5-pyrazolone and benzoyl chloride in the presence of aluminium chloride or by the Schotten-Baumann method), long needles, m. p. 128° , which is converted by bromine in glacial acetic acid solution into 4-bromo-5-benzoyl-1-benzoyl-3-methylpyrazole, long needles, m. p. 167° . 4-Phenyl-1-*p*-tolyl-3-methyldipyrzole, $\text{N}\begin{smallmatrix} \text{N}(\text{C}_6\text{H}_4\text{Me})\cdot\text{C}\cdot\text{NH} \\ \text{CMe} \end{smallmatrix}\text{---C}\cdot\text{CPh}\gg\text{N}$ (from 5-chloro-4-benzoyl-1-*p*-tolyl-3-methylpyrazole and hydrazine hydrate at $160\text{--}175^\circ$), colourless, matted needles, m. p. 244° . 1:3:4-Triphenyldipyrzole, $\text{N}\begin{smallmatrix} \text{NPh}\cdot\text{C}\cdot\text{NH} \\ \text{CPh}\cdot\text{C}\cdot\text{CPh} \end{smallmatrix}\gg\text{N}$, needles, m. p. 233° . H. W.

The Action of Diazomethane on the Ureides and Uric Acid. J. HERZIG (*Z. physiol. Chem.*, 1921, 117, 13—27).—A number of ureides and uric acids were methylated with diazomethane. Alloxan yielded a syrupy substance, $\text{C}_4\text{N}_2\text{O}_3\text{Me}\cdot\text{OMe}$. From barbituric acid, a crystalline substance, $\text{NMe}\begin{smallmatrix} \text{CO}\cdot\text{CH} \\ \text{CO}\cdot\text{NMe} \end{smallmatrix}\gg\text{C}\cdot\text{OMe}$, m. p. $164\text{--}166^\circ$, was obtained. Diethylbarbituric acid yielded an oily substance,

$C_8H_{11}N_2O_3Me$, which, after several months, crystallised in needles, m. p. 33–36°. Phenylethylbarbituric acid gave a compound,



a crystalline mass, m. p. 88–90°, dipropylbarbituric acid gave a crystalline compound, $C_{10}H_{14}O_3N_2Me_2$, m. p. 80–83°, uric acid gave a tetramethyl uric acid, $C_5O_3N_4Me_4$, the four methyl groups being attached to nitrogen. On treating barbituric acid with methyl sulphate in sodium hydroxide, a compound, $C_4H_2O_3N_2Me_2$, probably $CO \begin{smallmatrix} < NMe \cdot CO \\ NMe \cdot CO > \end{smallmatrix} CH_2$, m. p. 119–121°, was obtained.

S. S. Z.

Pyrimidines from Alkylmalonic Esters and Aromatic Amidines. ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1922, **44**, 361–366).—Alkyl malonic esters readily condense with aromatic amidines in the presence of sodium ethoxide, the monoalkylmalonic esters yielding insoluble yellow pyrimidine derivatives and the dialkyl esters giving soluble colourless derivatives. The colour of the derivatives from the monoalkyl esters is thought to be due to a tautomeric rearrangement to a compound

of the structure $CR \begin{smallmatrix} < C(OH) \cdot N \\ C(OH) \cdot N > \end{smallmatrix} CR'$. With two exceptions, the

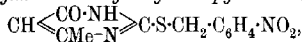
5-monoalkyl derivatives of pyrimidine all melt at above 300°, whereas the 5:5-dialkyl derivatives melt considerably below 300°. The pyrimidine derivatives described are all analogous to 4:6-diketot-2-phenyl-5:5-diethyltetrahydropyrimidine and are:

Substituents.			Substituents.		
5-Carbon.	2-Carbon.	M. p.	5-Carbon.	2-Carbon.	M. p.
	Methyl	>300°	Ethyl	<i>p</i> -Tolyl	>300°
Phenyl	Methyl	>300°	Ethyl	<i>p</i> -Ethoxyphenyl	>300°
Benzyl	Methyl	>300°	Dimethyl	Phenyl	184°
	Phenyl	>300°	Diethyl	Phenyl	207°
Methyl	Phenyl	>300°	Dipropyl	Phenyl	164°
Ethyl	Phenyl	>300°	Dibutyl	Phenyl	144°
Allyl	Phenyl	288–289°	Dibenzyl	Phenyl	224°
Butyl	Phenyl	296–297°	Diethyl	<i>p</i> -Tolyl	181°
<i>iso</i> -Amyl	Phenyl	>300°	Diethyl	<i>p</i> -Ethoxyphenyl	165°
Benzyl	Phenyl	>300°	Diethyl	β -Naphthyl	178°
Dimethyl	Phenyl	263°			

W. G.

Pyrimidines. XCI. Alkylation of 2-Thiopyrimidines.

WILLIAM JOHN HORN (*J. Amer. Chem. Soc.*, 1921, **43**, 2603–2611).—Experiments are described showing further abnormalities in the alkylation of 2-thiopyrimidines (cf. Johnson and Haggard, *A.* 1915, i, 88; Johnson and Moran, 1916, i, 78). A study has now been made of the alkylation of 2-*p*-nitrobenzylthiol-4-methyl-dihydro-6-pyrimidone. With methyl iodide substitution in the 1-position first occurs, and then this compound apparently forms an additive product with another molecule of methyl iodide. With ethyl bromide or allyl bromide, however, the action is quite different, oxygen ethers being formed in each case and there is no indication of substitution of the alkyl groups on a nitrogen atom of the ring.

2-p-Nitrobenzylthiol-4-methyldihydro-6-pyrimidone,

m. p. 220°, is obtained by the action of *p*-nitrobenzyl chloride on the sodium salt of 2-thio-4-methyluracil. When treated with the calculated amount of methyl iodide in the presence of sodium methoxide, it yields 2-*p*-nitrobenzylthiol-1:4-dimethyldihydro-6-

pyrimidone, $\text{CH} \begin{array}{c} \text{CO}\cdot\text{NMe} \\ \diagup \quad \diagdown \\ \text{CMe} \text{---} \text{N} \end{array} \text{C}\cdot\text{S}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, m. p. 136°, which

is hydrolysed by hydrochloric acid, giving 1:4-dimethyluracil and *p*-nitrobenzylmercaptan, m. p. 58°. By further alkylation, this dimethyl derivative gave an additive compound, some of which was also isolated from the products of the first alkylation. Its

constitution is apparently $\text{CH} \begin{array}{c} \text{CH}(\text{OMe})\cdot\text{NMe} \\ \diagup \quad \diagdown \\ \text{CMe} \text{---} \text{N} \end{array} \text{C}\cdot\text{S}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$,

and on hydrolysis it gives 1:4-dimethyluracil and *p*-nitrobenzyl sulphide, m. p. 126·5°, the latter being formed by oxidation due to the presence of a trace of free iodine.

With ethyl bromide the sodium salt of 2-*p*-nitrobenzylthiol-4-methyldihydro-6-pyrimidone gives 6-ethoxy-2-*p*-nitrobenzylthiol-4-

ethylpyrimidine, $\text{CH} \begin{array}{c} \text{C}(\text{OEt})\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{CMe} \text{---} \text{N} \end{array} \text{C}\cdot\text{S}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, m. p. 104°;

on hydrolysis, this yields 4-methyluracil. In a similar manner with allyl bromide, 6-allyloxy-2-*p*-nitrobenzylthiol-4-methylpyrimidine, m. p. 77–78°, is obtained.

Strakosch's observation (*Ber.*, 1872, 5, 698) giving the m. p. 140° for *p*-nitrobenzyl mercaptan is incorrect (see above) and a repetition of his work did not yield any of this mercaptan. W. G.

Colouring Matters from 1:2:4:5-Tetrahydroxybenzene and Related Substances. DHIRENDR NATH MUKERJI (*T.*, 1922, 121, 545–552).

The Cyanine Dyes. IV. Cyanine Dyes of the Benzothiazole Series. WILLIAM HOBSON MILLS (*T.*, 1922, 121, 455–466).

Ring Closure with Hydrazinedicarbonamides containing sulphur. II. Thiourazole. F. ARNDT, E. MILDE, and F. SCHEENSCHER (*Ber.*, 1922, 55, [B], 341–356; cf. Arndt and Milde, *ibid.*, 1921, i, 813).—Further investigation has established the general validity of the rule that ring closure with hydrazinedicarbonamides containing sulphur takes place in neutral or acid media by means of the sulphur atom, with formation of thiodiazoles, whereas in alkaline solution it occurs through the nitrogen atom, thus giving diazoles.

The hydrazide, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$, loses successively aniline, ammonia, and hydrogen sulphide when boiled with sodium hydroxide solution. The first change constitutes the main reaction and leads to the production of thiourazole, $\text{NH} \begin{array}{c} \text{CO}\cdot\text{NH} \\ \diagup \quad \diagdown \\ \text{CS} \text{---} \text{NH} \end{array}$, which forms colourless crystals, m. p. 206° (decomp.). The substance is most

conveniently isolated from the products of the reaction as the monosodium salt (the trihydrate and anhydrous substance are described) from which free thiourazole is readily obtained by addition of acid. Elimination of ammonia gives 4-phenylthio-

urazole, $\text{NPh} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \diagdown \quad \diagup \\ \text{CS} \cdot \text{NH} \end{smallmatrix}$ (see later), but the product derived by

loss of hydrogen sulphide has not been isolated in this connexion. The constitution of thiourazole is established by the formation of a dark yellow tri-silver salt, $\text{C}_2\text{ON}_3\text{SAg}_3$, by its oxidation by iodine in alco-

holic solution to thiourazole disulphide, $\begin{smallmatrix} \text{NH} \cdot \text{N} \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{NH} \end{smallmatrix} > \text{C} \cdot \text{S} \cdot \text{S} \cdot \text{C} < \begin{smallmatrix} \text{N} \cdot \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$

colourless, lustrous needles, m. p. 246° (decomp.) (the dihydrate is also described), and by the conversion of its monosodium salt by means of methyl sulphate into thiourazole methyl ether,

$\text{NH} \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \diagdown \quad \diagup \\ \text{C}(\text{SMe}) \cdot \text{N} \end{smallmatrix}$, colourless, anhydrous plates, m. p. $192\text{--}193^\circ$.

The substance described by Freund (A., 1894, i, 97; 1895, i, 400) as thiourazole is actually iminothiodiazolone, $\text{S} \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \diagdown \quad \diagup \\ \text{C}(\text{NH}) \cdot \text{NH} \end{smallmatrix}$ (cf. Busch and Schmidt, A., 1913, i, 907; Busch and Lotz, A., 1915, i, 317).

[With FRL. BIELICH.]—Thiourazole is more conveniently prepared by the action of boiling sodium hydroxide solution on the hydrazide, $\text{SMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_2$; the latter, a colourless, crystalline powder, m. p. 208° (decomp.), is obtained by the action of methyl chlorothioformate on thiosemicarbazide in warm aqueous solution.

3-Imino-4-phenylurazole, $\text{NPh} \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \diagdown \quad \diagup \\ \text{C}(\text{NH}) \cdot \text{NH} \end{smallmatrix}$, colourless, lustrous leaflets, m. p. $231\text{--}232^\circ$, is obtained readily and exclusively by the action of boiling alkali hydroxide on phenylhydrazothiodicarbonyl S-methyl ether, $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{C}(\text{NH}) \cdot \text{SMe}$, colourless, silky needles, m. p. indefinite 147° (decomp.).

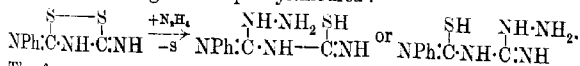
The hydrazide, $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, small, lustrous needles, m. p. 198° , is prepared by the action of semicarbazide hydrochloride on phenylthiocarbimide in aqueous alcoholic solution; it is converted by boiling alkali hydroxide solution almost exclusively into 4-phenylthiourazole (see above), long, coarse, colourless prisms ($+1\text{H}_2\text{O}$), m. p. (anhydrous) 196° . 4-Phenylthiourazole disulphide, needles, m. p. $284\text{--}285^\circ$, is most conveniently prepared by the oxidation of 4-phenylthiourazole with iodine in alcoholic solution. 4-Phenylthiourazole methyl ether crystallises in colourless, lustrous needles, m. p. $207\text{--}208^\circ$. The hydrazide, $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, is transformed by methyl sulphate and sodium hydroxide into the corresponding S-methyl ether which could not be obtained in the crystalline form; it is converted by boiling hydrochloric acid into phenylthiourazole methyl ether and by boiling sodium hydroxide

solution into anilurazole, $\text{NH} \begin{smallmatrix} \text{C}(\text{NPh}) \cdot \text{NH} \\ \diagdown \quad \diagup \\ \text{CO} \text{---} \text{NH} \end{smallmatrix}$, small, colourless, anhydrous crystals, m. p. 238° .

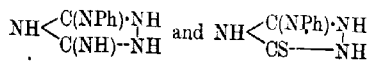
The *hydrazide*, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$, lustrous leaflets, m. p. 180° , is prepared from thiosemicarbazide and phenylthiocarbimide in aqueous-alcoholic solution. It is converted by boiling alkali hydroxide solutions with loss of ammonia and hydrogen sulphide into 4-phenyldithiourazole, $\text{NPh}\begin{smallmatrix} \text{CS}\cdot\text{NH} \\ \text{CS}\cdot\text{NH} \end{smallmatrix}$, colourless, coarse crystals, m. p. 216° (decomp.) (the substance described previously in the literature as 4-phenyldithiourazole is anilinothiodiazolethiol), and 3-imino-4-phenylthiourazole, m. p. $267\text{--}268^\circ$ (the *monohydrate*, colourless needles, is also described). Both substances are acidic, but can be largely separated from one another with the aid of sodium carbonate solution, in which practically only phenyldithiourazole is soluble. The latter substance is transformed by methyl sulphate in dilute ammoniacal solution into 4-phenyldithiourazole dimethyl ether, $\text{NPh}\begin{smallmatrix} \text{C}(\text{SMe})\cdot\text{N} \\ \text{C}(\text{SMe})\cdot\text{N} \end{smallmatrix}$, long, lustrous needles, m. p. $132\cdot5^\circ$ (the corresponding *nitrate* has m. p. 141°); it is oxidised by potassium ferricyanide in the presence of sodium hydroxide or by an alcoholic solution of iodine to a mixture of *products*, one of which, yellow crystals, m. p. 228° , gave analytical results in agreement with the formula $\text{C}_{16}\text{H}_{12}\text{N}_6\text{S}_4$. 3-Imino-4-phenylthiourazole is converted by methyl sulphate and sodium hydroxide into the corresponding *methyl ether*, m. p. 168° (the *hydrate*, $2\text{C}_6\text{H}_5\cdot\text{N}_4\text{S}_2\cdot\text{H}_2\text{O}$, silky needles, is also described); it behaves somewhat anomalously when oxidised, since it is stable towards iodine in alcoholic solution, but is affected by potassium ferricyanide in the presence of ammonia or sodium hydroxide; probably, however, a disulphide is not thereby formed, since the same phenomena are observed with the methyl ether.

H. W.

Disulphides with Neighbouring Single and Multiple Linkings. Syntheses of Triazoles and Thiodiazoles. EMIL FROMM, with ERICH KAYSER, KARL BRIEGLEB, and ERICH FÖHRENBACH (*Annalen*, 1922, **426**, 313—345).—The course followed by the reaction between bases and unsaturated disulphides of the type $\text{XCR}\cdot\text{S}\cdot\text{S}\cdot\text{CR}\cdot\text{Y}$ is, in general, that expressed by the equation $\text{XCR}\cdot\text{S}\cdot\text{S}\cdot\text{CR}\cdot\text{Y} + \text{NH}_2\text{Ph} \rightarrow \text{X}\cdot\text{CR}\cdot\text{SH} + \text{NHPh}\cdot\text{CR}\cdot\text{Y} + \text{S}$. The present paper shows that the reactions between hydrazines and similar disulphides are of an analogous kind and may be utilised for the synthesis of triazoles and thiodiazoles. For instance, phenyldithiobiuret may react with hydrazine in two ways, eliminating one atom of sulphur and yielding either aminophenylguanidinothiourea or aminoguanidinophenylthiourea:



The former can pass into a triazole by elimination of either H_2S or NH_3 , but the latter can give only the first of the two following substances:



3-amino-5-anilino-1:2:4-triazole and 3-thio-5-anilino-1:2:4-triazole.

The principal product is actually 3-thio-5-anilino-1:2:4-triazole, which separates from hot water in needles, m. p. 268°. This shows that the main product of the initial ring-scission is the aminophenylguanidinothiourea. The by-products obtained are 3-amino-5-anilino-1:2:4-triazole, which has m. p. 77° and gives a *mono-benzoyl* derivative of m. p. 142°, the salt, m. p. 70°, of the amino-anilinothiazole (basic constituent) with the thioanilinothiazole (acid constituent), and aminoguanidinophenylthiourea, which has m. p. 155° and yields a *benzylidene* derivative crystallising in yellow needles, m. p. 223°. The thioanilinothiazole gives a *dibenzoyl* derivative (yellow needles, m. p. 130°), and on treatment with benzyl chloride and alkali yields 5-anilino-3-benzylthiol-1:2:4-triazole, which has m. p. 168° and gives a *dibenzoyl* derivative, m. p. 108°. On oxidation by means of ferric chloride, the thioanilinothiazole gives a yellow *disulphide*, $S_2(C \begin{smallmatrix} \text{N} \cdot \text{N} \\ \text{NH} \end{smallmatrix} > C \cdot NHPH)_2$, m. p. 225°, which undergoes fission by means of sodium hydroxide, giving 3-hydroxy-5-anilino-1:2:4-triazole, m. p. 169° (the *dibenzoyl* derivative has m. p. 166°), and 3-thio-5-anilino-1:2:4-triazole. Aniline effects a similar fission, the products being the same thioanilinothiazole and 3:5-dianilino-1:2:4-triazole, which is conveniently isolated in the form of its *dibenzoyl* derivative, m. p. 88°.

The action of phenylhydrazine on perthiocyanic acid has already been investigated by Fromm and Schneider (A., 1906, i, 714) and has been shown to proceed in directions analogous to the reactions described above, the products being 3:5-dithio-1-phenyl-1:2:4-triazole and 3-amino-5-thio-1-phenyl-1:2:4-triazole. The former compound is now subjected to a closer investigation with the view of establishing its constitution quite definitely. On methylation by methyl iodide and sodium hydroxide, it forms 3:5-dimethylthiol-1-phenyl-1:2:4-triazole, filamentous needles, m. p. 73·5°, which on oxidation by permanganate yields 3:5-dimethyldisulphon-1-phenyl-1:2:4-triazole, filamentous needles, m. p. 182°, together with a substance, $C_{10}H_{11}O_2N_3S_2$, m. p. 104·5°, which may be either a monosulphone or a disulphoxide. The disulphone is unstable towards alkalis and loses one sulphone group, yielding 5-hydroxy-3-methylsulphone-1-phenyl-1:2:4-triazole, m. p. 206°, identical with the substance obtained on oxidising Acree's 5-hydroxy-3-methylthiol-1-phenyl-1:2:4-triazole (A., 1904, i, 351) by means of permanganate. 5-Hydroxy-3-methylsulphone-1-phenyl-1:2:4-triazole can be methylated by means of its silver salt, giving 5-methoxy-3-methylsulphone-1-phenyl-1:2:4-triazole, which separates from alcohol in fine needles, m. p. 206°. The disulphone, in contrast to its behaviour towards alkalis, is very stable towards acids, and can be nitrated with the formation of 3:5-dimethylsulphone-1-nitrophenyl-1:2:4-triazole, m. p. 238°, which with alkalis is converted into a substance, 5-hydroxy-3-methylsulphone-1-nitrophenyl-1:2:4-triazole, m. p. 234°, identical with the product obtained on directly nitrating hydroxymethylsulphonephenyltriazole.

Some derivatives of 3-amino-5-thio-1-phenyl-1:2:4-triazole are described also. 3-Amino-5-methylthiol-1-phenyltriazole, needles, m. p. 148°, is obtained with the help of methyl iodide and alkali; on benzylation in the presence of pyridine, it yields 3-benzoyl-amino-5-methylthiol-1-phenyl-1:2:4-triazole, m. p. 141.5°, which may also be obtained by methylating Fromm and Sturm's 5-thiol-3-benzoylamino-1-phenyl-1:2:4-triazole (A., 1913, i, 204). A dibenzoyl derivative, m. p. 152°, is formed when 3-amino-5-methylthiol-1-phenyltriazole is heated with benzoyl chloride until hydrogen chloride is no longer evolved.

The simplest members of the series to which the above substances belong are 3:5-dithiol-1:2:4-triazole, $\text{NH} \begin{smallmatrix} \text{C}(\text{SH})\text{:N} \\ \text{C}(\text{SH})\text{:N} \end{smallmatrix}$, and 5-amino-

3-thiol-1:2:4-triazole, $\text{NH} \begin{smallmatrix} \text{C}(\text{SH})\text{=N} \\ \text{C}(\text{NH}_2)\text{:N} \end{smallmatrix}$, which are both obtained as their hydrazine salts when hydrazine hydrate is allowed to react with perthiocyanic acid. They may be separated by taking advantage of the fact that the monothiol compound is the weaker acid and is liberated in the free condition when an aqueous solution of its hydrazine salt is evaporated. The hydrazine salt of the dithiol compound is stable in these circumstances, but may be decomposed by means of mineral acids or by benzaldehyde. 5-Amino-3-thiol-1:2:4-triazole separates from water in small, white needles, m. p. 298° (decomp.); 3:5-dithiol-1:2:4-triazole, m. p. 196° (decomp.), has strongly reducing properties; it first reddens blue litmus paper and then bleaches it, and quickly reduces iodine, ferric chloride, and ferricyanide; it gives a yellow lead salt, $\text{C}_2\text{H}_3\text{N}_2\text{S}_2\text{Pb}$, and a hydrazine salt, $\text{C}_2\text{H}_3\text{N}_2\text{S}_2$, m. p. 268° (decomp.). On benzylation by the Schotten-Baumann method, aminothioltriazole gives 5-amino-3-thion-2:4-dibenzoyl-1:2:4-triazole, yellow crystals, m. p. 178°, whilst the dithioltriazole yields 3:5-dithion-1:2:4-tribenzoyl-1:2:4-triazole, m. p. 171°, which on treatment with benzyl chloride and sodium hydroxide gives 3:5-dibenzylthiol-1:2:4-triazole, m. p. 112° (its hydrochloride has m. p. 157°), the product of the direct benzylation of dithioltriazole. The dibenzyl compound, on benzylation by the Schotten-Baumann method, yields 4-benzoyl-3:5-dibenzylthiol-1:2:4-triazole, which forms fine, white needles, m. p. 91°. The tribenzoate is readily hydrolysed by alkalis, all three benzoyl groups being eliminated. All these reactions are in harmony with the constitutions assigned to the original condensation products.

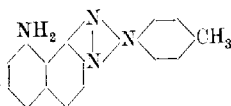
An investigation of the substances, $\text{C}_2\text{H}_3\text{N}_2\text{S}_2$ and $\text{C}_2\text{H}_3\text{N}_2\text{S}$, obtained by Freund and Imgart (A., 1895, i, 400) from hydrazo-dicarbonyldithioamide leads the present authors to the conclusion that these substances are not triazoles, but thiodiazoles, $\text{S} \begin{smallmatrix} \text{CS} \text{---} \text{NH} \\ \text{C}(\text{NH})\text{:NH} \end{smallmatrix}$ and $\text{S} \begin{smallmatrix} \text{C}(\text{NH}_2)\text{:N} \\ \text{C}(\text{NH}_2)\text{:N} \end{smallmatrix}$, isomeric, therefore, with the substances obtained

from perthiocyanic acid and hydrazine. 5-Amino-3-thion-4:1:2-thiodiazole forms a lead salt, $\text{C}_4\text{H}_3\text{N}_6\text{S}_2\text{Pb}$, and on benzylation gives 5-amino-3-thion-2:5-dibenzoyl-4:1:2-thiodiazole, m. p. 224°;

on benzylation, fission of the ring occurs and *benzyl benzylthiol-ψ-carbazinocarbothioxyate*, $C_7H_7 \cdot S \cdot C(NH_2) \cdot N \cdot N \cdot C(OH) \cdot S \cdot C_7H_7$, is produced. This substance forms palm-leaf-like crystals, m. p. 193° , and on benzylation gives an *anhydro-benzoate*, $CPh \leftarrow \begin{matrix} N \cdot C(S \cdot C_7H_7) \cdot N \\ O \cdot C(S \cdot C_7H_7) \cdot N \end{matrix}$

m. p. 123° , which may also be obtained by benzylating the above dibenzoyl compound. Freund and Imgart's melting points for 5-amino-3-thio-4 : 1 : 2-thiodiazole and 3 : 5-diamino-4 : 1 : 2-thiodiazole are revised to $228-235^\circ$ and 210° respectively. C. K. I.

Aminonaphthatriazoles as Colour Intermediates. GILBERT T. MORGAN and HUGH GILMOUR (*J. Soc. Chem. Ind.*, 1922, 41, 61—62r).—To compare it with 6-amino-2-*p*-tolyl- $\alpha\beta$ -naphthatriazole (this vol., i, p. 181), the corresponding 9-aminotriazole (accompanying



formula) was prepared. 8-Nitro- β -naphthylamine was coupled with toluene-*p*-diazonium chloride, forming 1-*p*-toluenazo-8-nitro- β -naphthylamine, dark red prisms, m. p. $177-178^\circ$. When oxidised with chromium trioxide in glacial acetic acid solution, this gave 9-nitro-2-*p*-tolyl- $\alpha\beta$ -naphthatriazole, yellow needles, m. p. 187° . By reduction with stannous chloride and hydrochloric acid in acetic acid solution, 9-amino-2-*p*-tolyl- $\alpha\beta$ -naphthatriazole hydrochloride was obtained, minute yellow needles decomposing at 220° . The 9-aminotriazole is much more reactive than the 6-isomeride, as it condenses readily with *p*-nitrobenzenediazonium chloride to give an aminoazo-derivative which can again be diazotised and coupled with β -naphthol or its sulphonic acids.

Both 5-nitro- and 8-nitro- β -naphthylamines when coupled with *p*-nitrobenzenediazonium chloride yield triazoles which on reduction give respectively 6- and 9-amino-2-*p*-aminophenyl- $\alpha\beta$ -naphthatriazole. The hydrochlorides of these are readily diazotised, and the resulting bisdiazonium salts couple readily with naphthol-sulphonic acids to form disazo-dyes. 6-Nitro-2-*p*-nitrophenyl- $\alpha\beta$ -naphthatriazole crystallises from acetic acid in minute yellow needles, m. p. $242-243^\circ$; 6-amino-2-*p*-aminophenyl- $\alpha\beta$ -naphthatriazole hydrochloride forms microscopic, yellow spicules decomposing at 300° ; the free base shows an intense green fluorescence in alcoholic and ethereal solution. 9-Nitro-2-*p*-nitrophenyl- $\alpha\beta$ -naphthatriazole separates from glacial acetic acid in yellow needles, m. p. $270-271^\circ$; 9-amino-2-*p*-aminophenyl- $\alpha\beta$ -naphthatriazole hydrochloride forms yellow needles readily soluble in hot water.

E. H. R.

7 : 9-Dialkyldeoxyuric Acids. I. HEINRICH BILTZ (*Annalen*, 1922, 426, 237—246).—7 : 9-Dialkyl-8-thiouric acids, which are obviously incapable of being converted into xanthines by the method previously employed (Biltz and Strufe, A., 1921, i, 612) and cannot readily be converted into the uric acids by oxidation, pass, in treatment with mild oxidising agents, into substances termed deoxyuric acids, containing one atom of oxygen less than

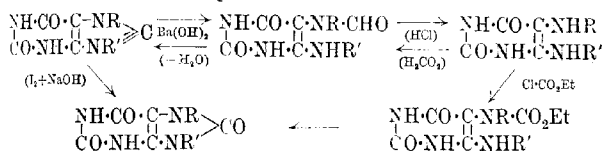
the corresponding uric acids. They are more strongly basic than the uric acids and are characterised by forming sparingly soluble salts with the acid HI_3 . A convenient method of preparation consists in oxidising by means of iodine a solution of the sodium salt of the 7:9-dialkyl-8-thiouric acid, rendered alkaline by sodium hydrogen carbonate; usually the periodide of the deoxyuric acid is precipitated. Nitrous acid also converts the thiouric acid into the deoxyuric acid.

The deoxyuric acids are very stable substances; in acid and in alkaline solution they are remarkably resistant to oxidising and reducing agents. However, the product obtained by the action of chlorine water gives the murexide test with ammonia, and the periodide when heated with sodium hydroxide decomposes, with the formation of a moderate quantity of the corresponding dialkyluric acid, from which it appears that the residue,

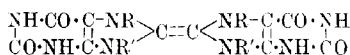
$$\begin{array}{c} \text{NH}\cdot\text{CO}\cdot\text{C}\cdot\text{NR} \\ | \quad | \\ \text{CO}\cdot\text{NH}\cdot\text{C}\cdot\text{NR} \end{array} > \text{C} <$$

must exist in the deoxyuric acid. With aqueous barium hydroxide hydrolysis occurs; the product is a formyldialkyldiaminouracil, from which the formyl group may be eliminated with the aid of hydrochloric acid. The free dialkyldiaminouracil may be re-formylated, using formic acid, and the formyl compound dehydrated with the formation of the original deoxyuric acid. If the dialkyldiaminouracil is treated with chloroformic ester, a urethane is produced, from which the uric acid may be prepared by the usual means.

These reactions are represented as follows:



The constitution suggested for the deoxyuric acids is a remarkable one, inasmuch as it involves a quinquivalent nitrogen and the presence of a triple linking in a ring, but it appears not to be without analogy. Possibly the above formula should be changed to

$$\begin{array}{c} \text{NH}\cdot\text{CO}\cdot\text{C}\cdot\text{NR} \\ | \quad | \\ \text{CO}\cdot\text{NH}\cdot\text{C}\cdot\text{NR} \end{array} > \text{C} <$$


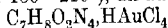
is out of the question by reason of the molecular weight and on obvious chemical grounds.

C. K. I.

7:9-Dialkyldioxyuric Acids. II. 7:9-Dimethyldioxyuric Acid. HEINRICH BILTZ and HANS BÜLOW (*Annalen*, 1922, 426, 246–263; cf. preceding abstract).—7:9-Dimethyl-8-thio-ψ-uric acid is readily prepared from 7-methyluramil and methylthiocarbimide. It separates from warm water in four-sided prisms, m. p. 224°

(corr.; decomp.), after sintering at 215°. A small amount of 7:9-dimethyl-8-thiouric acid is formed as a by-product in this condensation, and may be obtained in good yield from the ψ -uric acid by boiling with 10% hydrochloric acid. It forms needles which dissolve in about 600 parts of boiling water and melt with decomposition at 362°.

7:9-Dimethyldeoxyuric acid may be prepared from the thiouric acid by either of the general methods previously described. It is soluble in about 4 parts of boiling water, from which it separates in needles which decompose at 385°. It has the stability and general properties characteristic of its class (preceding abstract) and forms a hydrochloride (decomp. 345–350°), a perchlorate (decomp. 270°), an acid sulphate (decomp. 265°), a nitrate (decomp. 205°), an iodide (decomp. 350°), a periodide, $C_7H_9O_2N_4HI_3$, dark brown needles (decomp. 180–210°), an aurichloride,



(decomp. 286–296°), a platinichloride, and an additive product with silver nitrate (? $2C_7H_9O_2N_4AgNO_3$). 7:9-Dimethyldeoxyuric acid is converted by heating with sulphur into 7:9-dimethyl-8-thiouric acid, and by iodine and alkali hydroxides into 7:9-dimethyluric acid. 6-Methylamino-5-formylmethylaminouracil (decomp. 385°) can be crystallised from about 20 parts of boiling water, or from acetic acid, but in the latter case $2CH_3CO_2H$ is retained. 5:6-Dimethyldiaminouracil crystallises from acetic acid (with $2CH_3CO_2H$) as rhombic plates, m. p. 380° (decomp.), and gives a hydrochloride which decomposes at 261°. The methyl carbamate obtained from 5:6-dimethyldiaminouracil and methyl chloroformate, dissolves in 60 parts of boiling water and decomposes at 343°. The ethyl ester is soluble in 10 parts of boiling water and decomposes at 325°.

C. K. I.

7:9-Dialkyldeoxyuric Acids. III. 7-Methyl-9-ethyldeoxyuric Acid. HEINRICH BILTZ and HANS BÜLOW (*Annalen*, 1922, 426, 264–269; cf. preceding abstracts).—7-Methyl-9-ethyl-8-thio- ψ -uric acid, prepared from 7-methyluramil and ethylthiocarbimide, forms hexagonal tablets, decomp. 206° (corr.). The thiouric acid dissolves in about 400 parts of boiling water, from which it separates in silky needles, decomp. 359°. 7-Methyl-9-ethyldeoxyuric acid crystallises with $2H_2O$ as leaflets, decomp. 325° (corr.), and gives a hydrochloride, decomp. 277–278° (corr.); an iodide, decomp. 254° (corr.); a periodide, $C_8H_{10}O_2N_4HI_3$, decomp. 215° (corr.); an aurichloride, $C_8H_{10}O_2N_4HAuCl_4$, decomp. 190°, and a complex salt with silver nitrate. All these compounds are similar to the lower homologues previously described. C. K. I.

7:9-Dialkyldeoxyuric Acids. IV. 9-Methyl-7-ethyldeoxyuric Acid. HEINRICH BILTZ and DOROTHEA HEIDRICH (*Annalen*, 1922, 426, 269–283; cf. preceding abstracts).—9-Methyl-7-ethyl-8-thio- ψ -uric acid, leaflets, m. p. 212° (decomp.), is difficult to isolate owing to the ease with which it undergoes conversion into 9-methyl-7-ethyl-8-thiouric acid, silky filamentous crystals, decomp. 344° (corr.). 9-Methyl-7-ethyldeoxyuric acid, separates

from water with $2\text{H}_2\text{O}$ in rectangular leaflets, decomp. 340° (corr.), and gives a *hydrochloride*, decomp. 263° (corr.); an *iodide*, decomp. 251° (corr.); a *periodide*, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\text{HI}_2$, decomp. $215\text{--}222^\circ$ (corr.); a *periodide*, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\text{HI}_3$, decomp. $230\text{--}235^\circ$ (corr.); a *perchlorate*, decomp. 238° (corr.); a *nitrate*, decomp. 194° (corr.); an *aurichloride*, decomp. 239° (corr.), and a complex salt with potassium tri-iodide, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\text{S}_3\text{KI}_3$, decomp. 242° (corr.). 6-*Methylamino-5-formylethylaminouracil*, best obtained by using lime-water in place of baryta, forms hexagonal crystals, decomp. 262° , and is extremely soluble in water. 6-*Methylamino-5-ethylaminouracil*, forms long needles, m. p. 235° (decomp.), gives a *hydrochloride*, $\text{C}_7\text{H}_{12}\text{O}_2\text{N}_4\text{HCl}$, decomp. 280° (corr.), and a *methyl carbamate*, m. p. 326° (decomp.), on condensation with methyl chloroformate. 9-*Methyl-7-ethyluric acid*, forms small, lancet-like leaflets, m. p. 355° (corr., decomp.), and on treatment with chlorine and water yields 4 : 5-*dihydroxy-9-methyl-7-ethyl-4 : 5-dihydrouric acid*, which crystallises as small elongated prisms, m. p. 240° (decomp., corr.). 4-*Hydroxy-5-methoxy-9-methyl-7-ethyl-4 : 5-dihydrouric acid*, m. p. 131° (corr.), and 4-*hydroxy-5-ethoxy-9-methyl-7-ethyl-4 : 5-dihydrouric acid*, m. p. 193° , are prepared from the uric acid by means of chlorine and methyl or ethyl alcohol.

C. K. I.

7 : 9-Dialkyldeoxyuric Acids. V. 1 : 7 : 9-Trimethyldeoxyuric Acid. HEINRICH BILTZ and HANS BÜLOW (*Annalen*, 1922, 426, 283—290; cf. preceding abstracts).—1 : 7 : 9-*Trimethyl-8-thio-ψ-uric acid* is readily prepared by condensation of 1 : 7-dimethyluramil with methylthiocarbimide. It forms small, thick crystals, decomp. 185° , and on heating with hydrochloric acid passes into 1 : 7 : 9-*trimethyl-8-thiouric acid*, m. p. 317° (corr.), which may also be obtained from 7 : 9-dimethylthiouric acid by methylation with the help of methyl sulphate.

1 : 7 : 9-*Trimethyldeoxyuric acid* separates from water in small, rhombic leaflets, with $1\text{H}_2\text{O}$, m. p. 348° (corr., decomp.), and forms a *hydrochloride*, filamentous needles, decomp. 231° (corr.), an *iodide*, glistening, rectangular leaflets, decomp. 249° (corr.), a *periodide*, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\text{HI}_3$, sinters at 208° , a *nitrate*, sinters at 125° , and an *aurichloride*, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\text{HAuCl}_4$, needles, decomp. 267° (corr.). 6-*Methylamino-5-formylmethylamino-3-methyluracil*, forms rectangular tablets which sinter at 267° and evolve water vapour, leaving a residue consisting of 1 : 7 : 9-trimethyldeoxyuric acid. C. K. I.

7 : 9-Dialkyldeoxyuric Acids. VI. 1 : 3 : 7 : 9-Tetramethyldeoxyuric Acid. HEINRICH BILTZ and DOROTHEA HEIDRICH (*Annalen*, 1922, 426, 290—299; cf. preceding abstracts).—1 : 3 : 7 : 9-*Tetramethyl-ψ-uric acid*, decomp. 165° (corr.), is prepared from 1 : 3 : 7-trimethyluramil and methylthiocarbimide, or, alternatively, from 7 : 9-dimethyl-8-thio-ψ-uric acid by methylation with methyl sulphate. It passes very easily into 1 : 3 : 7 : 9-*tetramethylthiouric acid*, which forms fine needles, m. p. $255\text{--}258^\circ$ (decomp., corr.). Methylation of 1 : 3 : 7-trimethyl-8-thiouric acid by means of methyl sulphate and sodium hydroxide leads to the

formation of the 8-methylthiol ether, m. p. 179—180° (corr.), which appears to possess no tendency to pass into the isomeric C-methyl derivative.

1:3:7:9-Tetramethyldeoxyuric acid, m. p. 282° (corr.), forms a hydrochloride, m. p. 110—115° (corr.), a perchlorate, decomp. 237° (corr.), an iodide, decomp. 238° (corr.), and a periodide, $C_9H_{12}O_2N_4HI_3$, m. p. 195° (corr.), and on hydrolysis by barium hydroxide yields 6-methylamino-5-formylmethylamino-1:3-dimethyluracil, which separates from alcohol as small, elongated prisms, decomp. 259—260° (corr.). 5:6-Dimethylamino-1:3-dimethyluracil, decomp. 290° (corr.), is unstable in the presence of air and moisture. It forms a hydrochloride, prisms, decomp. 278° (corr.). These compounds are related like their analogues previously described.

C. K. I.

7:9-Dialkyldeoxyuric Acids. VII. 7:9-Diethyldeoxyuric Acid. HEINRICH BILTZ and HANS BÜLOW (*Annalen*, 1921, 426, 299—305; cf. preceding abstracts).—7:9-Diethyl-8-thio- ψ -uric acid (prepared from 7-ethyluramil and ethylthiocarbimide), forms leaflets, decomp. 208° (corr.). 7:9-Diethyl-8-thiouric acid, decomp. 340—369°, is sparingly soluble in boiling water, and does not give the murexide reaction. 7:9-Diethyldeoxyuric acid separates with $1H_2O$ from water as rectangular leaflets, decomp. 305—307°, and forms an iodide, rectangular leaflets, m. p. 262° (corr., decomp.), a periodide, $C_9H_{12}O_2N_4HI_2$, brown needles, m. p. 225° (corr., decomp.), and an aurichloride, $C_9H_{12}O_2N_4HAuCl_4$, decomp. 180—190°. 6-Ethylamino-5-formylethylaminouracil, forms needles which decompose at 268° (corr.), eliminating water and leaving a residue consisting of the original deoxyuric acid.

C. K. I.

9-Methyl-8-iodo- $\Delta^{7:8}$ -isoxanthine. HEINRICH BILTZ and HANS BÜLOW (*Annalen*, 1922, 426, 306—312; cf. preceding abstracts).—The sulphur atom in 9-methyl-8-thiouric acid is removed by iodine and sodium hydrogen carbonate, the product being a polyiodide of 8-iodo-9-methyl- $\Delta^{7:8}$ -isoxanthine, which is obtained in the free state on subsequent reduction by sulphurous acid. It separates from 800—900 parts of hot water in short, thick crystals which begin to lose iodine at 280°. It forms an ammonium salt, $C_9H_8O_2N_4I \cdot NH_4 \cdot 2H_2O$, and a di-iodide, $C_9H_8O_2N_4I_2$, and on reduction by means of stannous chloride gives 9-methyl- $\Delta^{7:8}$ -isoxanthine, which is conveniently isolated in the form of its stannichloride, $(C_9H_8O_2N_4)_2 \cdot H_2SnCl_4$.

Methylation of 9-methyl-8-thiouric acid by means of methyl sulphate and potassium hydroxide leads to the formation of 8-methylthiol-9-methyl- $\Delta^{7:8}$ -isoxanthine, which forms fine needles or four-sided leaflets, decomp. 335° (corr.).

C. K. I.

Oxonium Salts of Azo-substances. F. KEHRMANN and R. VAN DER LAAR (*Ber.*, 1922, 55, [B], 511—512).—*p*-Azoanisole unites slowly with acid-free methyl sulphate at 55—60°, yielding violet crystals which dissolve in water; addition of perchloric acid to the aqueous solution precipitates the corresponding perchlorate,

$C_{15}H_{11}N_2ClO_6$, dark red leaflets with a violet, metallic glance, from which the *platinichloride*, $(C_{15}H_{11}O_2N_2Cl)_2PtCl_4$, is obtained as a tile-red, crystalline powder. The constitution of the perchlorate is in all probability represented by the formula $OMe \cdot C_6H_4 \cdot NMe(ClO_4) : N \cdot C_6H_4 \cdot OMe$; the oxonium formula, $OMe \cdot C_6H_4 \cdot N^+ : N \cdot C_6H_4 \cdot OMe_2^+ ClO_4^-$, is improbable, but the quinonoid expression, $OMe \cdot C_6H_4 \cdot NMe : N \cdot C_6H_4 \cdot O < \overset{Me}{ClO_4}$, is not disproved. *p*-Azo phenetole gives precisely similar salts. H. W.

Preparation of *o*-Hydroxyazo-colouring Matters. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (F.P. 22347; from *Chem. Zentr.*, 1921, iv, 1067—1068).—Diazotised anthranilic acid is combined with pyrazolones containing a hydroxyl group in the aryl portion of the molecule, or diazotised aromatic amines which do not contain a hydroxyl or carboxyl group in the ortho-position to the amino-group are combined with pyrazolones containing a hydroxyl or carboxyl group in the aryl portion of the molecule. Colouring matters are obtained:—From *o*-diazotised anthranilic acid and 1-5'-sulpho-2'-hydroxyphenyl-3-methyl-5-pyrazolone-3'-carboxylic acid, $CO_2H \cdot C_6H_2(SO_3H)(OH) \cdot C_3N_2H_2O$ (from 5-sulpho-2-hydroxy-1-hydrazinobenzene-3-carboxylic acid and ethyl acetoacetate). From diazotised chloroanthranilic acid ($NH_2 : CO_2H : Cl = 1 : 2 : 4$) and 1-5'-chloro-3'-sulpho-2'-hydroxyphenyl-3-methyl-5-pyrazolone (from 5-chloro-3-sulpho-2-hydroxy-1-hydrazinobenzene and ethyl acetoacetate). From diazotised sulphanthranilic acid ($NH_2 : CO_2H : SO_3H = 1 : 2 : 5$) and 1-5'-nitro-2'-hydroxyphenyl-3-methyl-5-pyrazolone (from 5-nitro-2-hydroxy-1-hydrazinobenzene and ethyl acetoacetate). From diazotised sulphanthranilic acid and 1-4'-hydroxyphenyl-3-methyl-5-pyrazolone-3'-carboxylic acid. From diazotised sulphanilic acid and 1-4'-hydroxyphenyl-3-methyl-5-pyrazolone-3'-carboxylic acid. From diazobenzene and 1-5'-chloro-2'-hydroxyphenyl-3-methyl-5-pyrazolone-3'-carboxylic acid. From *m*-diazobenzoic acid and 1-5'-sulpho-1'-hydroxyphenyl-3-methyl-5-pyrazolone-3'-carboxylic acid. From 1-diazonaphthalene-5-sulphonic acid and 1-4'-hydroxyphenyl-3-methyl-5-pyrazolone-3'-carboxylic acid. 5-Chloro-2-hydroxy-1-phenylhydrazine-3-carboxylic acid (obtained by reduction of diazotised 4-chloro-2-amino-1-hydroxybenzene-6-carboxylic acid) gives with ethyl acetoacetate 1 : 5'-chloro-2'-hydroxyphenyl-3-methyl-5-pyrazolone-3'-carboxylic acid. Most of the compounds obtained are fast yellow dyes. G. W. R.

The Preparation of Optically Active Hydrazines. II. The Preparation of *dl-p*-sec.-Butylphenylhydrazine. The Resolution of *dl-p*-sec.-Butylaniline. J. W. E. GLATTFELD and EDGAR WERTHEIM (*J. Amer. Chem. Soc.*, 1921, 43, 2682—2687; cf. A., 1921, i, 63).—*dl-p*-sec.-Butylaniline was obtained by reducing *dl-p*-nitro-sec.-butylbenzene with tin and hydrochloric acid. It has b. p. 112°/11 mm., and gives an acetyl derivative, m. p. 125—126° (cf. Reilly and Hickinbottom, T., 1920, 117, 120). The racemic butylaniline was resolved into its optically active components by converting it into its camphorsulphonates and separating these by

recrystallisation first from ether and then from a mixture of ethyl acetate and acetone. The l-p-sec.-butylaniline has b. p. 116.5–118°/15 mm. and gives an acetyl derivative, m. p. 123–124°, $[\alpha]_D^{25} + 0.9301^\circ$. d-p-sec.-Butylaniline has b. p. 123–125°/20 mm., $[\alpha]_D^{25} + 0.26^\circ$.

dl-p-sec.-Butylaniline was diazotised and the resulting product poured into a cold solution of sodium sulphite, giving a rich red solution. This was reduced by zinc and acetic acid and ultimately dl-p-sec.-butylphenylhydrazine was isolated having b. p. 155–157°/18 mm. and giving a hydrochloride, a sodium sulphonate, and a crystalline derivative with d-galactose, m. p. 152–153°. Attempts to reduce the active butylanilines in a similar way were not successful.

W. G.

The Coagulation of Protein by Sunlight. ELRID GORDON YOUNG (*Proc. Roy. Soc.*, 1922, [B], **93**, 235–248).—Sunlight or the arc light when freed from ultra-violet and infra-red rays can effect coagulation of serum-albumin and ovalbumin when these have been recrystallised several times. The process consists of two separate reactions, (1) denaturation, (2) flocculation. During the primary reaction there is an increase of viscosity and specific rotation and a decrease of surface tension, and at the same time a convergence of the reaction of the solution towards neutrality independent of its initial P_H . Serum-albumin is much more easily affected than ovalbumin. The rôle of light is similar to that of heat—catalysis of the primary reaction. Addition of certain substances, for instance potassium thiocyanate or alcohol, accelerate the reaction.

H. K.

Deaminoproteins. J. HERZIG and HANS LIEB (*Z. physiol. Chem.*, 1921, **117**, 1–12).—Deaminoglutin, deamino-ovalbumin, deaminocasein, and deaminogliadin yield, when treated by the Van Slyke and Sørensen methods, approximately the same amount of amino-nitrogen as the respective proteins from which they are derived.

S. S. Z.

Ultramicroscopic Investigation of Casein. B. BLEYER and R. SEIDL (*Kolloid Z.*, 1922, **30**, 117–118).—An ultramicroscopic examination and comparison of calciumcasein and paracasein and of acid casein and acid paracasein. In the case of the calcium derivatives, it is shown that the Brownian movement of the paracasein compound is twice as rapid as that of the casein calcium compound. The individual particles of the paracasein compound are always smaller than those of the casein compound. This indicates that the viscosity of paracasein solutions will be considerably smaller and the electrical conductivity larger than in corresponding solutions of casein, a result which confirms the work of Laqueur and Sackur. It also supports Van Slyke's view that the molecular weight of paracasein is only half that of casein. The acid derivatives were prepared by shaking 1 gram of casein or paracasein with 100 c.c. of N/100 hydrochloric, sulphuric, lactic or acetic acid. On examination in the luminous beam, it is found

that the particles are much larger than in the case of the calcium derivatives. As in the case of the calcium derivative, the casein particles are in more rapid motion than the corresponding paracasein particles. The lactic acid casein and hydrochloric acid casein particles are in the most rapid motion, but in all cases except lactic acid the velocity decreased markedly after keeping for twenty-four hours. The acid caseinates are shown to be adsorption complexes and not true chemical compounds. J. F. S.

Crystallisation of Hæmoglobin. G. AMANTEA and C. KRZYSZKOWSKY (*Arch. Fisiol.*, 1920, **18**, 87—92; from *Chem. Zentr.*, 1921, iii, 1324).—Crystallisation of hæmoglobin from the blood of many animals can easily be effected if hæmolysis is produced by saponaria-saponin (not, however, with human blood and blood of frogs and toads). The hæmoglobin of nucleated corpuscles is crystallised with difficulty. Addition of gum arabic to red corpuscles may induce the formation of hæmoglobin crystals. G. W. R.

Pigment Metabolism. I. FROMHOLDT and NERSESSOV (*Biochem. Z.*, 1921, **125**, 149—152).—Bilirubin prepared from a number of different sources and analysed by Pregl's method for carbon and hydrogen, and nitrogen by that of Kjeldahl, gave values in agreement with the accepted formula. H. K.

The "Coupled" Nucleic Acid from the Pancreas. II. LINAR HAMMARSTEN and ERIK JORPES (*Z. physiol. Chem.*, 1922, **18**, 224—232).—The nucleic acid from the pancreas previously described by Hammarsten yields guanylic acid and a substance which consists of a pentose and most probably of only one purine base, namely, adenine, on alkaline hydrolysis. In the authors' opinion, this reaction is characteristic of a nucleic acid resembling yeast-nucleic acid. S. S. Z.

The Isoelectric Point of Collagen. ARTHUR W. THOMAS and MARGARET W. KELLY (*J. Amer. Chem. Soc.*, 1922, **44**, 195—201).—The swelling method of determining the isoelectric point of American hide powder as the source of collagen is applicable only for the purpose of locating the approximate isoelectric region when solutions of widely differing hydrogen-ion concentrations are employed, and consequently large swelling differences are obtained. The dye method gives more consistent results, the values of p_H at the isoelectric point varying from 4.6 to 5.4, with an average of 5.0. The results indicate that hide substance, generally referred to as collagen, is a mixture of proteins rather than one simple protein. The isoelectric points of a number of different proteins, as reported in the literature, are tabulated. W. G.

The Significance of the Isoelectric Point for the Preparation of Ash-free Gelatin. JACQUES LOEB (*J. Amer. Chem. Soc.*, 1922, **44**, 213—215; cf. *A.*, 1919, i, 295, 296, 418; ii, 14, 399, 497).—A reply to Smith (cf. *A.*, 1921, i, 749). W. G.

The Drying and Swelling of Gelatin. S. E. SHEPARD and F. A. ELLIOTT (*J. Amer. Chem. Soc.*, 1922, **44**, 373—379).—A preliminary note in which the authors consider the behaviour of

gelatin in "leaf" form and in cubes on ordinary "forced" drying and subsequent swelling. They conclude that the "case-hardening" effect, in particular as initiated at edges and corners, is responsible for two important phenomena in the hydration-dehydration cycle of gelatin jellies. The first, noted with "leaf" gelatin, is that the greatest shrinking and subsequent swelling takes place perpendicularly to the largest evaporating surface (cf. Shreve, A., 1919, i, 228). The second is the apparent influence of the original concentration of the gelatin jelly on its swelling limit subsequent to drying. This they regard as due to the initial case-hardening, which preserves an approximate "skin extension" corresponding with the original figure. On this basis, any structure is not inherent in the gelatin, but is an environmental impress, a strain structure in the original mass.

W. G.

Swelling and Gelation of Gelatin. ROBERT H. BOGUE (*J. Ind. Eng. Chem.*, 1922, 14, 32—35).—When gelatin sols and gels are treated with sodium silicates of varying composition, the swelling and the viscosity increase with a decrease in the silica content and appear to be dependent on the p_H value, as this increases constantly with increase of the ratio $Na_2O : SiO_2$. The swelling and viscosity reach their maximum at p_H 8.5, and decrease slightly at higher values; the jelly consistence, however, is solid at p_H values between 4.7 and 8.0, but becomes soft at 8.5 and is liquid at 9.0.

W. P. S.

Movement of Pepsin in Agar-agar Gels with and without Protein. C. A. PEKELHARING (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, 24, 269—279).—Pepsin (A., 1902, i, 411) from the gastric mucosa of pigs diffuses more rapidly in agar-agar gels containing proteins than in similar gels to which no protein has been added or which contain mixed amino-acids. The movement of pepsin through gels containing protein is held to be due to alternate combination of the enzyme with the protein substrate and decomposition of the substrate with liberation of the enzyme. This view is supported by the fact that in gels specially purified from nitrogenous substances, diffusion of pepsin is slower than in ordinary agar-agar gels.

G. W. R.

Uniformity in Invertase Action. J. M. NELSON and DAVID I. HITCHCOCK (*J. Amer. Chem. Soc.*, 1921, 43, 2632—2655).—From a consideration of the results of Nelson and Vosburgh (cf. A., 1917, ii, 252) and new data recorded, it is shown that all preparations of yeast invertase are not alike in their action, but that some of them are abnormal in allowing the hydrolysis of sucrose to slow more than others after the first 20% of the inversion. The following empirical equation has been deduced, which fits the experimental data for the hydrolysis of sucrose by normal invertase over an extreme range of invertase concentration of 12 : 1.

$$t = 1/n [\log 100/(100 - p) + 0.002642p - 0.000008860p^2 - 0.0000001034p^3]$$

where t is the time, p the percentage of sucrose inverted and n is a

constant which is proportional to the amount of active invertase present. It is shown that the hydrolysis-time curves for normal invertase are of the same shape for these different invertase concentrations and can be made to superimpose if the time scale be multiplied by the proper constant. The hydrolysis curve with normal invertase has the same shape at temperatures varying from 15° to 35°, and at hydrogen-ion concentrations from 4.0×10^{-5} to 3.2×10^{-7} .

One abnormal invertase preparation could be rendered normal by the addition of boiled normal invertase or of 0.1M-sodium chloride, but another was not affected by such treatment. Further dialysis or partial inactivation by heating or by submission to ultra-violet light did not render normal invertase preparations abnormal.

W. G.

The Law of Action of Saccharase : Velocity of Hydrolysis and Reaction of the Medium. H. COLIN and (Mlle) A. CHAUDUN

(*Compt. rend.*, 1922, 174, 218—220; cf. A., 1918, i, 414; ii, 357).—In extension of the view that the inversion of sucrose by saccharase is a catalytic action in which the catalyst transitorily unites with the substance which it decomposes, the velocity of formation of the intermediate compound being infinitely great with respect to the velocity of decomposition, it is suggested that there is a weight, a , of sucrose which corresponds with a volume, n , of a given saccharase solution. It is shown that this, like the velocity of inversion, varies with the reaction of the medium, the value of a being smaller the greater is the acidity of the medium. Thus the addition of acid may be considered as causing a diminution of the amount of enzyme coming into action, and when the diminution of velocity due to this cause becomes greater than the increase in velocity due to the greater instability of the complex, the variation of the velocity becomes negative, that is, the velocity of inversion diminishes.

W. G.

The Inversion of Sucrose by Saccharase. (Mlle) ANDRÉE CHAUDUN (*J. fabr. sucre*, 1921, 62, No. 39).—The rate of inversion of sucrose by saccharase was studied. To a sucrose solution of known strength, a known amount of saccharase was added. At fifteen minute intervals the amount of invert-sugar formed was estimated in an aliquot part of the solution. When the enzyme was used in excess the rate of inversion decreased from the start, the values found agreeing with the law of Wilhelmy, $x = a(1 - e^{-kt})$, where x is the weight of sucrose inverted during the time t , a the initial concentration of sucrose, and e and k are constants. When the sucrose was used in excess and the solution was not more than 10% in strength, the rate of inversion remained constant until a point B was reached where the sucrose and enzyme were present in equivalent amounts, then decreased according to the above law. In more concentrated solutions, a very slight decrease in the rate of inversion was noticed before the point B was reached. Other investigators have ascribed this to a supposed reversibility of the reaction, but it is here considered to be due to the hindering

of the reaction by the increase in viscosity as the inversion progresses.

CHEMICAL ABSTRACTS.

Inhibition Phenomena in Amylases. II. URBAN OLSSON (*Z. physiol. Chem.*, 1921, **117**, 91—145).—The optimum reaction for the action of a sample of ptyalin in the presence of sodium chloride and sodium acetate was found to be $P_H=6.4$. Malt diastase is inactivated more readily than ptyalin. Iodine and fluorine ions have no inactivating influence on malt diastase. Ferric chloride in low concentration activates, in higher concentrations inactivates malt diastase. On dialysing ptyalin, an activator is removed which consists chiefly of salts the presence of which is necessary for the usual diastatic action. The action of various inhibiting reagents is given. It is suggested that the inactivating capacity of some of the heavy metals might be utilised as a means of detecting very small traces of these metals.

S. S. Z.

Emulsin. BURCKHARDT HELFERICH (*Z. physiol. Chem.*, 1921, **117**, 159—171).—A satisfactory method for preparing emulsin from the kernel of the plum is to mill the stones, extract the paste with water under toluene for nine weeks, filter, and precipitate with 95% alcohol. Prolonged extraction and precipitation from dilute solution conduce to more potent preparations. The enzyme can be purified by dialysis. The conditions for the quantitative estimation of the activity of β -glucosidases is also described.

S. S. Z.

Emulsin. RICHARD WILLSTÄTTER and WILHELM CSÁNYI (*Z. physiol. Chem.*, 1921, **117**, 172—200).—The optimum reaction for the hydrolysis of amygdalin by emulsin lies in the neighbourhood of neutrality; that of lactose and raffinose more on the acid side. Emulsin preparations kept for about six months showed considerable loss of activity. From the difference of the quotients (a) of the hydrolysis of β -methylglucoside, lactose, and raffinose from that of amygdalin, (b) of the hydrolysis of lactose from that of prunasin, (c) of the hydrolysis of β -glucoside from that of prunasin by various preparations from sweet and bitter almonds and apricot kernels, it was concluded that the emulsin reactions were of the nature of independent enzyme reactions, and that the preparations were a mixture of numerous enzymes capable of degrading glucosides and polyoses.

S. S. Z.

Castor Bean Lipase, its Preparation and some of its Properties. D. E. HALEY and J. F. LYMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 2664—2670).—An active lipase preparation is best obtained from castor beans by extracting the crushed, hull-free beans with light petroleum. Lipase zymogen is activated by acid, but the active enzyme is unstable and is rapidly destroyed in an acid medium in the absence of fats. In the presence of fats, the enzyme shows much greater stability. The zymogen form appears to be somewhat soluble in fats or in a mixture of fat and ethyl ether, but is insoluble in ether alone. The optimum hydrogen-ion concentration for castor bean lipase is 1×10^{-5} . As the acidity

increases above this point, the lipolytic activity falls and stops entirely at a concentration of about 1×10^{-3} . The hydrolysis of hard fats by the castor bean lipase in the presence of water is accelerated by the addition of light petroleum. Similarly, the hydrolysis of oils is somewhat hastened.

W. G.

The Importance of the Medium in the Study of Catalase. I. UBALDO SAMMARTINO (*Biochem. Z.*, 1921, **126**, 179—188).—Experiments on the evolution of oxygen from hydrogen peroxide under the influence of a dilute solution of blood and addition of a vitamin solution, for example, extract of yeast, show that a mercury surface and addition of sodium hydrogen carbonate greatly influence the reaction velocity. Using the Van Slyke apparatus to avoid mercury, the presence of the vitamin solution, whether the reaction of the medium be faintly alkaline or made definitely alkaline by addition of sodium hydrogen carbonate or sodium hydroxide solution, has a strong accelerating influence on the evolution of oxygen. H. K.

Influence of Different Chemicals, of Kations and Anions, and of Mixtures of Electrolytes, on the Ureolitic Power of Urease. D. H. WESTER (*Pharm. Weekblad*, 1922, **59**, 173—190; *Biochem. Z.*, 1922, **128**, 279).—The enzyme was obtained by extraction with equal volumes of water and glycerol of the seeds of soja and canavalia beans, the solutions being stable. The course of the reaction was followed by titration of the ammonium carbonate formed, using *N*/10-acid and methyl-orange.

Tannin, iodine, and copper sulphate retard the action; chloroform, however, does not, and thymol, mercuric chloride, and oil of mustard have practically no effect in concentrations sufficient to inhibit bacterial growth. Alcohols also have only slight retarding effects. Of the common kations, Ca^{++} and Ba^{++} have relatively great effect, K^+ least; Mg^{++} is irregular. Of the anions, Cl^- , Br^- , and NO_3^- have almost equal effects, I^- greater and SO_4^{--} less. Mixtures of electrolytes exert almost the same effect as would be exerted by that which has the strongest effect if it were present alone.

S. I. L.

Organo-derivatives of Thallium. V. The Preparation of Thallium Diaryl Salts. ARCHIBALD EDWIN GODDARD and DOROTHY GODDARD (*T.*, 1922, **121**, 482—488).

Sodium 2-Nitro-4-hydroxymercuriphenoxide. J. F. SCHAMBERG, G. W. RAIZISS, and J. A. KOLMER (U.S. Pat. 1390972).—Sodium 2-nitro-4-hydroxymercuriphenoxide is formed when *o*-nitrophenol and aqueous sodium hydroxide react with an excess of mercuric acetate in dilute aqueous solution containing a little acetic acid at a temperature which is gradually raised from 50° to 80° . The product is soluble in hot water, has a brick-red colour, and possesses antiseptic and therapeutic properties.

CHEMICAL ABSTRACTS.

Physiological Chemistry.

Respiratory Metabolism and Toxic Glycæmia. A. BORN, STEIN and ELISABETH MÜLLER (*Biochem. Z.*, 1921, **126**, 64—76).—Experiments on dogs and man indicate that injections of pilocarpine cause an immediate increase in the respiratory coefficient. This is attributed to combustion of sugar. Adrenaline, however, although it forms sugar from glycogen, does not bring about increased sugar combustion. H. K.

The Degradation Products of Cholesterol in the Animal Organs. (Substances Associated with Cholesterol in the Blood.) I. LIFSCHÜTZ (*Z. physiol. Chem.*, 1921, **117**, 201—211).—Some derivatives of cholesterol are associated with it in the unsaponifiable fraction of fat in the blood. Some of these substances are precipitated by digitonin, whilst others are not. The chemical properties of both fractions are given. S. S. Z.

The Chemical Nature and the Transformation of the Fat of the Blood. I. LIFSCHÜTZ (*Z. physiol. Chem.*, 1921, **117**, 212—217).—On oxidation of the blood fat the relative proportion of the unsaponifiable matter increases whilst the ratio of crystalline cholesterol to cholesterol oxidation products diminishes. S. S. Z.

The Uric Acid of Human Blood. J. LUCIEN MORRIS and A. GARRARD MACLEOD (*J. Biol. Chem.*, 1922, **50**, 65—75).—Certain discrepancies between the results obtained in the estimation of uric acid in human blood by the authors' method (this vol., ii, 328) and 'by that of Folin and Wu (A., 1919, ii, 308) lead to the suggestion that there are two forms of uric acid present in human blood. E. S.

Blood Enzymes. I. Occurrence of Maltase in Mammalian Blood. ARTHUR COMPTON (*Biochem. J.*, 1921, **15**, 681—686).—Maltase is present in the blood-serum of the pig, dog, goat, sheep, rat, horse, and ox, and is absent from that of the cat, guinea-pig, rabbit, and man. The pig is particularly rich in the enzyme. Some variation occurs in different individuals belonging to the same species, especially in the case of the dog. W. O. K.

The Ferment Numbers of Blood. I. Quantitative Estimation of Catalase, Protease, Peroxydase, and Esterase in a Drop of Blood. A. BACH and SOPHIE ZUBKOWA (*Biochem. Z.*, 1921, **125**, 283—291).—The blood solution used for the estimations is prepared by measuring 0.02 c.c. of blood by means of a capillary pipette and adding to it 20 c.c. of water. For the estimation of catalase and protease, use is made of the observation that the action of catalase on hydrogen peroxide falls off with rise of temperature, due to the action of the protease on the catalase, so that the catalase number is the number of milligrams of hydrogen peroxide

decomposed by 0.001 c.c. of blood at 17°, and the protease number is the difference between the catalase numbers determined at 17° and 37°. In man, the catalase number varies between 14 and 18, and the protease number between 3 and 5.

As evidence for the existence of a peroxydase in blood, it is found that when blood is diluted 1000-fold, it accelerates the action of hydrogen peroxide on guaiacol, but is inactive when heated. The peroxydase number is the quantity of guaiacol in thousandths of a milligram oxidised by 0.001 c.c. of blood in presence of hydrogen peroxide. The guaiacol is determined colorimetrically. For estimation of esterase, use is made of the observation that guaiacol esters are not attacked by peroxydase except in the presence of esterase and the esterase number of the blood is the number in thousandths of a milligram of guaiacol eliminated from guaiacol esters by 0.001 c.c. of blood.

H. K.

The Fermentative Properties of Blood. V. Appearance of Ferments in Blood after Various Operations. LUDWIG PRICUSSEN (*Biochem. Z.*, 1921, 126, 93—96).—By transplantation of tissues or by interfering with the normal mechanism of the kidney of rabbits and dogs, the author finds evidence of the presence in the sera of specific proteolytic ferments. The results are in general complicated.

H. K.

Blood Clotting. IV. B. STUBER and A. FUNCK (*Biochem. Z.*, 1921, 126, 142—146).—Fibrinogen in 6% sodium chloride solution is precipitated by kations in the order $\text{Cs} > \text{K} > \text{Na} > \text{Li} > \text{Rb}$. Dialysed fibrinogen dissolved in sodium hydroxide or hydrochloric acid of various strengths is precipitated by alcohol when the alkali or acid concentration is above 0.05*N*, but there is no precipitation between the range 0.05*N* to 0.005*N*. Dialysed salt-free fibrinogen has an isoelectric point at P_H 5.0. In acid solution, fibrinogen is precipitated by anions in the order $\text{SO}_4 > \text{citrate} > \text{acetate} > \text{Cl} > \text{NO}_3, \text{Br} > \text{I} > \text{CNS}$. In alkaline solution, the bivalent kations are effective in the order $\text{Ba} > \text{Sr} > \text{Ca} > \text{Mg}$.

H. K.

Coagulation of the Blood. I. Some Physico-chemical Aspects of Coagulation. JOHN WILLIAM PICKERING and JAMES ARTHUR HEWITT (*Biochem. J.*, 1921, 15, 710—724).—The authors attempt to bring the facts known about the clotting of the blood into connexion with physico-chemical concepts. Alcohol precipitates a greater quantity of gelatin from solution when added slowly than when added all at once. This effect may help to explain the delay in coagulation following slow injection of tissue extracts or of synthetic colloids. In fact, a negative phase (delayed coagulation) can be obtained *in vitro* by adding tissue extract slowly to unsalted birds' blood. The authors suggest that the injected colloids combine with the fibrinogen, and that there is no necessity for assuming the existence of antithrombin. In the same way, the slow disintegration of the platelets of the normal circulating blood helps it to maintain its fluidity. There is no conclusive evidence that the liver produces an anti-coagulant.

Blood surrounded by paraffin exhibits an intermediate reversible phase in the formation of a clot. A gel is first formed, which dissolves in tap water. This phase lasts for only a few minutes in mammalian blood, but for a day or two in frogs' blood. At 37°, birds' blood clots rapidly in clean glass vessels without the addition of tissue extract.

It is suggested that coagulation phenomena are largely physical and colloidal in nature, and that the effect of foreign substances may be due largely to surface effects and to the electrical charges of the particles concerned. W. O. K.

Solubility of Carbon Monoxide in Serum and Plasma. H. R. O'BRIEN and W. L. PARKER (*J. Biol. Chem.*, 1922, **50**, 289—300).—The solubility of carbon monoxide is practically the same in ox, sheep, and human serum and in ox plasma, and is about three-quarters of its solubility in water. E. S.

Relation between the Viscosity of Blood and the Ratio of Uric Acid in Serum to that in Whole Blood. ROUZAUD and THIÉRY (*Compt. rend. soc. biol.*, 1921, **85**, 962—964; from *Physiol. Abstr.*, 1922, **6**, 626).—The viscosity of blood, which depends on the number of red cells, determines the distribution of uric acid between plasma and corpuscles. In patients with excessively viscous blood, the serum contains proportionally less uric acid than in patients with less viscous blood; in the latter, whether anæmic or hydræmic, the amount of uric acid in the serum may occasionally exceed that in the whole blood. E. S.

Relation between Viscosity and the Ratio of Cholesterol in Serum to that in Whole Blood. ROUZAUD and THIÉRY (*Compt. rend. soc. biol.*, 1921, **85**, 964—965; from *Physiol. Abstr.*, 1922, **6**, 627).—The ratio of cholesterol in the serum to that in whole blood varies directly with the viscosity. There is a larger fraction of cholesterol in the serum when the blood is rich, than when it is poor, in red cells. This is considered to be of importance in cases of hypercholesterinæmia. E. S.

The Action of Salvarsan on the Serum of Animals and on Blood-cells in Vitro. J. L. KRITSCHESKY (*Biochem. Z.*, 1921, **126**, 11—20).—Salvarsan in acid and in alkaline solution causes a pronounced decrease in the degree of dispersity of colloids, as is shown by its behaviour towards serum. Corpuscles of various species are strongly agglutinated to various degrees, depending on the species. The hæmolytic action of salvarsan is inhibited by serum. H. K.

Influence of Temperature on Hypotonic Hæmolysis. A. JARISCH (*Pflüger's Archiv*, 1921, **192**, 255—271; from *Physiol. Abstr.*, 1922, **6**, 625).—The resistance of the red cells to hæmolysis increases with rise of temperature between 0° and 45° to 50°, but then very rapidly falls off as temperatures are reached which are themselves capable of causing hæmolysis. Different animals vary in the sensitiveness to temperature influence on hypotonic hæmolysis; the differences are explained as dependent on different

phosphate content of the corpuscles, low phosphate content corresponding with a small temperature effect. By adding phosphate buffer mixtures to ox blood, the phosphate content of which is small, the temperature effect could be intensified. Sodium sulphate and sodium tartrate had no such effects. The phosphates probably act by keeping the hydrogen-ion concentration constant, so that with rise of temperature the concentration of hydroxyl ions increases. If the latter is kept constant by adding ammonium salts, the effect of temperature is diminished. E. S.

Basal Metabolism in Menstruation. MARION O. P. WILTSHIRE (*Lancet*, 1921, 201, 388—389).—Basal metabolism is not appreciably affected by menstruation. A. A. E.

Paradoxical Behaviour of the Sugar Metabolism on Simultaneous Administration of Pilocarpine and Adrenaline ("Dissimilatory Reversal"). R. VOGEL and A. BORNSTEIN (*Biochem. Z.*, 1921, 126, 56—63).—In the dog both adrenaline and pilocarpine cause an increase of blood-sugar. The simultaneous injection of both causes no change in the normal blood-sugar content. The mechanism of the two glycemias is supposed therefore to be different. H. K.

The Metabolism of Carbohydrates. II. On the Possible Occurrence of Stereochemical Changes in Equilibrated Solutions of Reducing Sugars Introduced into the Circulation. JAMES ARTHUR HEWITT and DAVID HENRIQUES DE SOUZA (*Biochem. J.*, 1921, 15, 667—671; cf. A., 1920, i, 508, 648).—From estimates of the optical rotation of the urine of rabbits or dogs after the intravenous injection of equilibrated solutions of dextrose, *d*-fructose, or *d*-galactose, it is concluded that the equilibrium of these sugars is unaltered as a result of their passage through the body and that no stereochemical changes take place.

The polarimetric estimations of the sugar in the urine do not agree with Bertrand estimations, and so the former method may give fallacious results if uncontrolled. W. O. K.

Influence of Radiation on Nucleic Acid Metabolism. LUDWIG PINCUSSEN and KATE MOMFERRATOS-FLOROS (*Biochem. Z.*, 1921, 126, 86—92).—Exposure to Röntgen rays increases the katabolism of purine derivatives as shown in rabbits by increased oxalic acid excretion and as shown in vitro by a change of optical rotation. H. K.

Accessory Food Factors. II. Importance of Water-soluble Extractives. RICHARD GRALKA and HANS ARON (*Biochem. Z.*, 1921, 126, 147—152; cf. A., 1921, i, 475).—Experiments on rats indicate that a lack of fat-soluble vitamin is borne much better if copious water-soluble extractives, as, for example, of carrots and bran, be added. H. K.

Chemistry of Blood and Spinal Fluid. GRETE EGERER-SERAM and C. E. NIXON (*Arch. Int. Med.*, 1921, 28, 561—585).—About one hundred spinal fluids were analysed with the following

results: Sugar (Myers-Bailey method), 0.045—0.095, average 0.069% in normal individuals; approximately the same in cases of syphilis, tabes, brain tumour, neurasthenia, arteriosclerosis, and other diseases; slightly increased in dementia paralytica and hysteria; decreased in tuberculous and epidemic meningitis and increased in diabetes with increase in blood-sugar; ratio of spinal fluid-sugar to blood-sugar variable in all groups. Creatinine, 0.45—2.20 mg. per 100 c.c. in patients without renal disease; ratio to blood creatinine very variable. Urea, 9.87 mg. per 100 c.c. or 62% of that in blood, both values slightly increased in cerebro-spinal syphilis. Titration to bromocresol-purple, 2.11—2.63, average 2.49 c.c. 0.1N HCl per 100 c.c. normal, practically the same in pathological cases except in acidosis and a few unexplained cases. Carbon dioxide capacity 46.5—61.7, average 53.1% normal, decreased in acidosis and few other cases; lipase present only in 2 out of 26 cases; trypsin, absent in all; diastase 22% of blood diastase, variations unrelated to sugar-content of fluid; d 1.0086.

CHEMICAL ABSTRACTS.

The Action of Potassium and Calcium Ions on the Surviving Human Stomach. OTTO TEZNER and MAX TUROLT (*Z. ges. exp. Med.*, 1921, **24**, 1—10).—The addition of calcium to Ringer solution inhibits stomach contractions. The inhibition is overcome by acetylcholine and barium chloride, but not by nicotine, and is probably due to stimulation of the sympathetic. The action of adrenaline is more marked in calcium-rich than in normal Ringer solution. The addition of potassium to Ringer solution increases automatic muscular action; this action is increased by papaverine, but not by atropine; with large doses it is increased up to muscle cramp. In addition to the action on the muscle, there is probably also a stimulation of the nerve-endings due to injury of the vasoconstrictors. Potassium behaves in every respect similarly to barium even in its antagonism to calcium. The addition of potassium does not affect the action of acetylcholine, but decreases adrenaline action. Calcium-free media produce a reduction of stomach motility, owing to diminished vagus sensitivity.

CHEMICAL ABSTRACTS.

Relation of Histamine to Intestinal Intoxication. I. Presence of Histamine in the Human Intestine. JONATHAN MEAKINS and CHARLES ROBERT HARRINGTON (*J. Pharm. exp. Ther.*, 1922, **18**, 455—465).—Histamine was demonstrated in minute concentration in the human caecum and transverse colon, but could not be detected in faeces possibly owing to oxidation during passage through the large intestine. The formation of histidine does not seem to depend on intestinal obstruction, and the amount present is too small to account for intestinal intoxication. G. B.

Pharmacology of Selenium and Tellurium. III. The Action of their Acids on the Organs of the Circulation. GEORG JOACHIMOGLU* and W. HIROSE (*Biochem. Z.*, 1921, **125**, 5—11).—On the isolated frog's heart, sodium tellurite is at least

two hundred times as toxic as sodium tellurate, and sodium selenite at least one hundred times as toxic as sodium selenate. The selenite is also much more toxic than the tellurite. The heart musculature has a reducing effect on the first three salts mentioned. On the rabbit's blood-pressure, sodium selenite and tellurite have a more powerful depressor action than sodium selenate and tellurate.

H. K.

Microchemical Recognition of Urea in the Kidney by means of Xanthidrol. H. STÜBEL (*Anat. Anz.*, 1921, **54**, 236—239).—Xanthidrol combines with urea to give insoluble crystalline dioxanthylurea. By means of this reaction the presence of urea can be demonstrated in tissue. The tissue is immersed in small pieces in a 6% solution of xanthidrol and acetic acid for six to twelve hours, washed in absolute alcohol for forty-eight hours, with repeated renewal of alcohol, the tissue cleared in xylene, embedded in paraffin, and treated as other histological preparations.

CHEMICAL ABSTRACTS.

Secretin. I. and II. C. VAN EWEYK and M. TENNENBAUM (*Biochem. Z.*, 1921, **125**, 238—245; 246—252).—I. Popielski's observation on the stimulating effect of histamine on the flow of pancreatic juice in a Pavlov dog is confirmed. Tyramine, glycine, alanine, and glutamic acid are without action. By heating histidine at 300°, an active stimulant was obtained which gave a picrate identified as histamine picrate. The amino-acids formed on hydrolysis of casein, when heated at 280° or 300° give an active substance, in all probability histamine.

II. The artificial secretin produced by the hydrolysis of spinach has no action on the blood pressure of the rabbit or on the isolated uterus of the guinea-pig, and is therefore not to be identified with histamine.

H. K.

Chemical Composition of the Thyroid Gland. EDGARD ZUNZ (*Arch. internat. Physiol.*, **16**, 288—306; from *Chem. Zentr.*, 1921, iii, 1329).—The mean weight of thyroid glands examined was 26 to 30 grams. The moisture content was 75—76%. On the material dried at 105°, the following results were obtained: nitrogen, 13.82%; ash, 3.53%; phosphorus, 0.55%; iodine, 0.2293%. (See also Zunz, *Arch. internat. Physiol.*, 1921, **15**, 459.)

G. W. R.

Spleen and Digestion. W. MOLLOW (*Z. physiol. Chem.*, 1921, **117**, 218—239).—Splenectionomy did not affect the digestion of dogs with gastric and duodenal fistulas.

S. S. Z.

The Pituitary Active Principles and Histamine. H. H. DALE and H. W. DUDLEY (*J. Pharm. expt. Ther.*, 1921, **18**, 27—42).—Contrary to the suggestion of Abel and Nagayama (*ibid.*, 1920, **15**, 347), the pituitary activity on the isolated uterus is almost completely destroyed by boiling with 0.5% hydrochloric acid. So little histamine is present in the gland, that its chemical identification is impracticable, and there seems no reason for

suggesting a relation between histamine and the specific action of pituitary extracts. The oxytocic principle (acting on the uterus) is slowly destroyed by crepsin, but not by papain (cf. *Ann. Reports*, 1920, 17, 172).
G. B.

Pressure of Carbon Dioxide or Swelling of Protein as the Cause of Muscle Contraction. OTTO FÜRTH (*Biochem. Z.*, 1921, 126, 55).—The author, in reply to Wacker (*ibid.*, 1921, 120, 284), reaffirms his position.
H. K.

Osmotic Behaviour of Frog's Muscle, Deficient in Water and Poisoned by Glycerol, and on the Shrinkage of Muscle Protein. PAUL DUX and ARTUR LÖW (*Biochem. Z.*, 1921, 125, 222—237).—The muscles of frogs which have lost 20% of their weight by drying, when placed in physiological saline solution, swell more rapidly and eventually lose weight more rapidly than normal muscle. The muscles of frogs which have been poisoned by glycerol show a still sharper rise and fall, the muscles of such frogs being about one-fifth the weight of normal muscle. This very steep rise is partly due to accumulation of lactic acid in the tissue robbed of water. The results are held to support Fürth's hypothesis of muscle contraction.
H. K.

The Interconversion of Carbohydrate and Lactic Acid in Muscle. DOROTHY LILIAN FOSTER and DOROTHY MARY MOYLE (*Biochem. J.*, 1921, 15, 672—680).—This paper confirms various recent investigations on the function of lactic acid in the muscle. Exhaustive stimulation results in a minimum lactic acid content. During recovery in oxygen after fatigue, there is an increase in carbohydrate content and a corresponding decrease in lactic acid, confirming Meyerhof's work in support of the view that the lactic acid formed during the first stage of excitation is partly reconverted back into carbohydrate during recovery. In chopped muscle, the decrease in carbohydrate is quite parallel to the increase in lactic acid and does not lag behind it as found by Parnas. Chopped muscle is able, not only to break down hexosephosphate, but also to synthesise it from dextrose and phosphate.
W. O. K.

The Distribution of Carnosine in the Animal Kingdom. WINIFRED MARY CLIFFORD (*Biochem. J.*, 1921, 15, 725—735).—Using the colorimetric method previously described by the author (*A.*, 1921, ii, 604), quantitative estimations have been made of the carnosine (β -alanylhistidine) in the muscles of a large variety of animals. It appears to be completely absent from the flesh of certain fishes, birds, and reptiles, but is present in all mammals so far examined, the highest figure being obtained in the case of the bull, the fresh muscle of which contains more than 1%. In some cases (for example, salmon) the colour is not developed properly owing apparently to the presence of some inhibitory substance, and in such cases the observations were controlled by precipitating and isolating the carnosine.
W. O. K.

The Rôle of Inorganic Salts in the Functions of the Cell. S. G. ZONDEK (*Ber. deut. Pharm. Ges.*, 1922, **32**, 7—15).—The inorganic salts in the living cell play an important part in the chemical mechanism by means of which it performs its functions. Apart from their functioning as catalysts, as, for example, iron as an oxygen carrier in hæmoglobin, attention is directed to the influence exerted by the ions, particularly the kations, on the cell colloids, including protoplasm. The determining factor in this case is not osmotic pressure, but the actual valency of the ions. Both univalent and multivalent kations alone inhibit the living functions, but if both are present together in suitable proportions, as, for example, sodium or potassium, and calcium as in Ringer's solution, then the poisonous action is removed (cf. this vol., i, 296). This antagonistic action of uni- and bi-valent kations is observable in the higher organisms, so, for example, sodium salts, and still more pronouncedly potassium salts, lead to a stoppage of an isolated frog's heart with relaxation of the muscles, whilst calcium salts lead also to a stoppage with contracted muscles. With a mixture of the two ions the heart's action remains normal. These phenomena are attributable to the physico-chemical influence which the respective ions exert on the colloidal state of the cell protoplasm.
G. F. M.

The Function of the Vitamins in the Chemistry of the Cell. W. R. HESS (*Z. physiol. Chem.*, 1921, **117**, 284—308).—The diminution in the respiratory function of polyneuritic pigeons can be demonstrated in vitro to be due to the decrease in the various tissues of the enzymes associated with respiration. The polyneuritic condition in birds can also be induced by inhibiting the respiratory functions of the tissues with hydrogen cyanide. Birds kept on a diet of polished rice were shown to be more susceptible to potassium cyanide intoxication than normal birds. S. S. Z.

Mode of Action of Potassium on Isolated Organs. A. J. CLARK (*J. Pharm. expt. Ther.*, 1922, **18**, 423—447).—Rubidium acts as a perfect and cesium as an imperfect substitute for potassium in all the isolated tissues examined (chiefly rabbit's auricle, frog's heart, uterus, intestine). Thorium and uranium do not act as substitutes to potassium, but act as irritants to the frog's heart and will induce automatic beats in hearts arrested by lack of potassium (cf. Zwaardemaker, A., 1917, i, 70, 105, 241; 1918, ii, 182; *Ann. Reports*, 1919, **16**, 148; Loeb, A., 1921, i, 145; Peters, A., 1921, i, 144).
G. B.

Copper in Tumours and Normal Tissues. CHARLES POWELL WHITE (*Lancet*, 1921, **201**, 701—703).—Copper was found to be present in all the animal and vegetable tissues examined, and to exist to a greater extent in degenerating tumours than in those which are not degenerated. The suggestion is made that copper may be of physiological importance in the higher animals and plants.
A. A. E.

New Observations on the Venom of Ants. ROBERT STUMPER (*Compt. rend.*, 1922, 174, 413—415; cf. *ibid.*, 1922, 174, 66).—The amount of formic acid in the venom from the ant, *Formica rufa*, varied from 21.35 to 72.8%. Formic acid is invariably found in the *Camponotinae*, but the *Myrmicinae* and the *Dolichoderinae* practically do not secrete this acid. The toxic action of the venom of the *Camponotinae* is due to formic acid and there are two distinct actions, namely, a corrosive action due to the concentration of the acid and the toxic action proper, due to an injurious influence of the formate ion on the nervous system. W. G.

An Organic Constituent of the Tube of *Mesochætopterus taylori*. Potts. C. BERKELEY (*J. Biol. Chem.*, 1922, 50, 113—120).—By extracting the tubes of *Mesochætopterus taylori*, a polychæte worm, with warm 2% sodium carbonate, a furfuraldehyde-yielding substance is obtained which resembles chondroitin-sulphuric acid. On hydrolysis, it yields sulphuric acid, a volatile organic acid, a hexosamine which is probably galactosamine, and probably glycuronic acid. E. S.

Origin of Milk Fat, and its Relation to the Metabolism of Phosphorus. EDMOND JOHN SHEEHY (*Biochem. J.*, 1921, 15, 703—709).—Carbohydrate and fat are equally efficient in the food of the cow for the production of milk fat. This indicates that the immediate source of the milk fat is some compound which can be produced from fat or from sugar, and may be a phosphatide. There is no parallelism between the quantity of phosphoric acid and of fat or caseinogen in milk, but this may be due to the inorganic phosphorus being partly returned to the blood from the mammary gland. W. O. K.

The Diastatic Action of Cow's Milk towards Various Starches. FERDINAND WELZMÜLLER (*Biochem. Z.*, 1921, 125, 179—186).—The diastatic action of cows' milk was determined at various temperatures on a number of varieties of starch. The results show that a diastase is present in cows' milk with an optimum temperature of 37°. This, together with its different behaviour towards a variety of starches, indicates a difference between the diastase of cows' milk and other diastatic ferments. H. K.

Ambard's Urea Constant. ALFRED LUBLIN (*Biochem. Z.*, 1921, 125, 187—201).—Experiments on the excretion of urea and urine in man in normal and pathological cases do not support Ambard's laws (*Compt. rend. Soc. Biol.*, 1910). H. K.

Influence of Lecithin on the Excretion of Veronal. C. BACHEM (*Biochem. Z.*, 1921, 126, 117—119).—After subcutaneous injection into rabbits of a mixture of lecithin and sodium veronal, the excretion of veronal in the urine is the same as when sodium veronal is injected alone. If, however, the lecithin be given intravenously and the sodium veronal subcutaneously, the excretion of veronal decreases by 33 to 50%. H. K.

Urochrome as a Derivative of Chlorophyll. HERBERT ELDON ROAF (*Biochem. J.*, 1921, 15, 687—688).—Consumption of green plant pigment (chlorophyll) increases the output of urochrome in the urine, whereas with carotene there is no such increase. W. O. K.

Alcaptonuria and its Metabolism. R. B. GIBSON and C. P. HOWARD (*Arch. Int. Med.*, 1921, 28, 632—637).—In a case of alcaptonuria, high values were obtained for ammoniacal nitrogen, uric acid nitrogen, and undetermined nitrogen, whilst the urea-nitrogen value was low. The excretion of sulphur appeared to be normal. CHEMICAL ABSTRACTS.

Inflammation. I. Influence of Chemicals on the Chemotaxis of Leucocytes in Vitro. ELIZABETH P. WOLF (*J. Expt. Med.*, 1921, 34, 375—396).—The calcium ion is the only inorganic ion which is found to be of itself positively chemotactic; the chemotaxis exhibited by magnesium and sodium salts is dependent on the negative ions. Sodium phosphates, morphine, amino-acids, and amines are positively, and all potassium salts negatively chemotactic; examples are also given of substances which act synergistically as regards chemotaxis. Although tyramine, for example, is an exception to the rule, it is suggested that the longer the carbon chain, the greater is the degree of chemotaxis. The conditions of the test appear markedly to influence the character of the results. CHEMICAL ABSTRACTS.

The Total Non-protein Nitrogen Constituents of the Blood in Chronic Nephritis with Hypertension. J. LISLE WILLIAMS (*Arch. Int. Med.*, 1921, 28, 426—433; cf. *ibid.*, 1921, 27, 748).—In chronic nephritis with hypertension, there is a retention of nitrogenous products in the blood and a diminished ability to excrete phenolsulphonaphthalein. The changes from the normal in these respects parallel the renal involvement but bear no definite relation to the increase in blood pressure. In cardiac insufficiency, without definite nephritis, there is a slight retention of nitrogenous products, particularly uric acid. Improvement in the cardiac condition is followed by a partial or complete return to the normal non-protein nitrogen of the blood. The presence of albumin and casts in the urine is not necessarily diagnostic of nephritis nor is their absence necessarily indicative of the non-existence of such disease. CHEMICAL ABSTRACTS.

Blood Chemistry in Puerperal Infection. PAUL COUINAUD and RENÉ CLOGNE (*Rev. mensuelle gynéc. et obstét.*, 1921, 3, 265—274).—In puerperal infection, blood urea is increased in proportion to the severity of the infection; the residual nitrogen of the blood is increased; in the urine, Lantzenberg's coefficient is increased, and the amount of urinary acetone is augmented as compared with values obtained in a normal puerperium. CHEMICAL ABSTRACTS.

Tetany. H. ELIAS and E. A. SPIEGEL (*Wiener Arch. Inn. Med.*, 1921, 2, 447—460).—The phosphorus content of the blood serum

is increased in tetany. The increase in total phosphorus depends on an increase in inorganic phosphorus, whilst the lipid phosphorus shows no characteristic change. In general, the phosphorus content shows a greater increase in the more severe cases of tetany. The change in phosphorus content cannot be attributed to increased muscular activity. A disturbance of phosphorus metabolism appears to be an important symptom of tetany, and is perhaps also an important factor in its occurrence.

CHEMICAL ABSTRACTS.

Pharmacology of Carbon Oxy-sulphide. RICHARD FISCHER (*Biochem. Z.*, 1921, **125**, 12—24).—The action of carbon oxy-sulphide was investigated on frogs and rabbits and on blood *in vitro*. The gas is unstable and readily forms hydrogen sulphide. The frog is relatively resistant, an atmosphere containing 4.5% of the gas causing death in one hour. In the case of the rabbit, inhalation of air containing less than 1% of the gas leads to death. In both cases death is due to respiratory failure. There is no apparent change in the blood *in vivo*; but *in vitro*, blood treated with carbon oxy-sulphide shows the absorption bands of thio-haemoglobin.

H. K.

[Physiological] Action of Dimethyl Telluride Dihaloids. DOUGLAS V. COW and W. E. DIXON (*J. Physiol.*, 1922, **56**, 42—52).—The stereoisomeric dimethyl telluride dichlorides, TeMe_2Cl_2 , described by Vernon (T., 1920, **107**, 86, 889) behave quite differently when injected intravenously into cats, dogs, or rabbits. The α - or *trans*-compound is relatively inactive, the β - or *cis*-compound is a powerful stimulant of the spinal medulla and specifically excites the adrenal gland to excrete adrenaline; hence it causes rise of blood pressure and other effects. This new type of the effect of stereochemical arrangement on physiological action is considered to be due to the intramolecular strain of the β -chloride. Ultimately both compounds are excreted in the breath as dimethyl telluride.

G. B.

Influence of Intravenous Sugar Injections on the Excretion of Lactic Acid, on the Blood-sugar, and on the White Blood-corpuscles. WACŁAW MORACZEWSKI and EGON LENDNER (*Biochem. Z.*, 1921, **125**, 49—68).—The authors have examined the effect of the administration of dextrose or levulose orally or intravenously on the blood-sugar, the urinary content of lactic acid, phosphoric acid, and sugars, the body temperature, and the corpuscular content (red and white) of the blood, both in the case of normal persons and in pathological cases. The effect of simultaneous administration of adrenaline and phloridzin was also examined, and the effect of injections of salvarsan, dextrin, deuterio-albumose, etc. In general, the results vary from case to case. There is no apparent relation between phosphate excretion and lactic acid excretion, and although injection of dextrose produces little effect, levulose causes a large increase of lactic acid in the

mine, a rise of body temperature of 3° , and a decrease of leucocytes. Phloridzin and adrenaline increase the lactic acid excretion.
H. K.

Behaviour of Oxalic Acid in the Animal Body. LUDWIG REICUSSEN (*Biochem. Z.*, 1921, 126, 82—85).—About four-fifths of the oxalic acid injected subcutaneously as sodium salt into rabbits appears in the urine. This quantity shows a slight decrease when the animal is exposed to light in the presence of an activator (eosin or dichloroanthracenedisulphonic acid).
H. K.

The Behaviour of some Cyclic Compounds in the Human and Animal Organisms. ERICH SCHEMPF (*Z. physiol. Chem.*, 1921, 117, 41—47).—Phenylacetic acid administered as the sodium salt to a cat was excreted in the urine as phenaceturic acid. The same compound given subcutaneously to a hen was excreted as a substance which did not quite agree with the properties of phenaceturic acid which Totani identified in similar circumstances. The sodium salt of *o*-nitrophenylacetic acid was excreted as the unchanged acid in the case of a man and a dog, as was also found to be the case with the *p*-nitro-compound except that a few decigrams of hippuric acid were also found in the human urine. Phenylchromoacetic acid in the case of man and dog was excreted as mandelic acid, whilst α -thiophenic acid was recovered in the urine in both cases as thiophenuric acid. A human patient who received pyromucic acid per os excreted it in the urine as pyromycuric and hippuric acids.
S. S. Z.

Action of Adrenaline on the Blood-sugar. GÉZA PETÉNYI and HEINRICH LAX (*Biochem. Z.*, 1921, 125, 272—282).—In man at all ages, subcutaneous administration of adrenaline produces a hyperglycæmia followed by a state of hypoglycæmia. In tetany, the behaviour is slightly different. The normal dextrose content shows greater variations and after adrenaline the hyperglycæmia is smaller and the hypoglycæmia more pronounced and protracted than in normal persons.
H. K.

Physiological Action of N-Methylhistamine and of Tetrahydropyrido-3:4-iminazole ("Iminazoleisopiperidin" of Fränkel) [1:3:5-Benztriazole]. H. H. DALE and H. W. HADLEY (*J. Pharm. expl. Ther.*, 1921, 18, 103—110).—4- β -Methylaminoethylglyoxaline (*N*-methylhistamine), prepared by Fargher and Pyman (*T.*, 1921, 119, 734), has 1/200 of the activity of histamine on the blood pressure and 1/80 of the activity of the ferus. The base prepared by Fränkel and Zeimer (*A.*, 1920, 1, 32) by condensing histamine with methylal by no means exceeds the latter base in activity, as was claimed by its discoverers, but is only 1/1500 of the activity of histamine on uterine muscle, and practically none on the blood pressure. The dihydrochloride melts at 276° — 278° , and not at 253° as stated by Fränkel and Zeimer, whose preparation must have been seriously contaminated with histamine.
G. B.

Pigment Metabolism. II. FROMHOLDT and NERSESSOV (*Biochem. Z.*, 1921, **125**, 153—157).—Bilirubin in quantities above 0.1 gram is lethal when injected intravenously into rabbits and causes excretion of albumin. With dogs and rabbits, repeated injection of bilirubin leads to urobilinuria and in the case of dogs bilirubin appears in the urine.
H. K.

The Influence of Treatment with Alkali or Bromine on the Physiological Activity and Foaming Capacity of some Saponaceous Substances. ERNST SIEBURG and FRANZ BACHMANN (*Biochem. Z.*, 1921, **126**, 130—141).—The biological activity of five saponaceous substances, cyclamin, digitonin, saponin pur. alb., Quillaia saponin, and Guaiak saponin, were compared before and after treatment with alkali or with bromine. As a rule, such treatment results in a depression of activity as exemplified by the property of foaming, by precipitation of cholesterol, by hæmolysis of corpuscles, by toxicity on the frog's heart, and by the toxicity on tadpoles. There is no close parallelism between these properties, except in the action on the frog's heart and the toxicity on tadpoles.
H. K.

Distribution of Chloride and Water after Poisoning with Mercuric Chloride. A. BORNSTEIN and JOH. KERR (*Biochem. Z.*, 1921, **126**, 120—129).—A comparison is made of the chloride and water-content of the blood, kidneys, liver, lungs, brain, intestine, muscles, skin, and skeleton of normal rats, and rats which have received, subcutaneously, either sodium chloride, sodium chloride and mercuric chloride, or cantharidin. There is no parallelism between water and chloride retention. For the ashing of animal tissues the Hoppe-Seyler-Thierfelder method can be shortened by stronger ignition in a muffle furnace without loss of chloride.
H. K.

Chemotherapy of Antimony. Comparison of Antimony Tartrates with Organic Compounds of Antimony. ROBERT GEORGE FARGHER and WILLIAM HERBERT GRAY (*J. Pharm. expt. Ther.*, 1921, **18**, 341—360).—The toxicity to mice of a number of salts of antimonyltartaric acid and of phenyl-, of *m*-acetylanilino-phenyl-, and of *p*-bromophenyl-stibinic acids has been determined. The paper contains a review of the literature of the chemotherapy of antimony, and describes a method for estimating antimony in organic compounds.
G. B.

Effect of Hydrogen-ion Concentration on the Toxicity of Alkaloids for *Paramæcium*. MARIAN M. CRANE (*J. Pharm. expt. Ther.*, 1921, **18**, 319—339).—The limits of P_H within which *Paramæcium* can live for twenty-four hours are 5—9.6. The effect of P_H on the toxicity of alkaloids varies with the dissociation constant of the latter, and the results seem to indicate that only the free undissociated base is toxic. Thus a change in P_H scarcely influences the toxicity of quinoline, whereas with strychnine, and piperidine, which have a much higher dissociation constant, the toxicity at P_H 5.9 is twenty-five times as great as at P_H 8.0. G. B.

Chemistry of Vegetable Physiology and Agriculture.

The Determination of Alkalinity in Culture Media. L. MICHAELIS (*Z. Immun.* 1921, **32**, 194–203).—A colorimetric method is described which indicates the p_H of culture media in a simple and rapid manner. The method differs from that of Clark and Lubs in that an indicator with a single change in colour, from colourless to yellow, is used. The reagent is a solution of 0.3 gram of *m*-nitrophenol in 100 c.c. of distilled water.

CHEMICAL ABSTRACTS.

The Ionisation Constants of Glycerophosphoric Acid and their Use as Buffers, especially in Culture Media. R. R. FELLOWS, S. F. ACREE, P. M. AVERY, and E. A. SLAGLE (*J. Infect. Dis.*, 1921, **29**, 1–6).—Disodium glycerophosphate is a solvent for some salts of calcium and magnesium and perhaps other metals, and when used in proper concentration prevents much of the objectionable precipitation of phosphates on the alkaline side of neutrality. This property suggests its employment in culture media, in the washing of agar, in the precipitation of casein, and for the study of the effect of the calcium and magnesium ions on the growth of various organisms. The fact that the ionisation constants of the glycerophosphates are substantially the same as those of the non-glycerolated phosphates makes possible a substitution of these salts as buffers, owing to their stability in the lower alkaline ranges where, for example, an initial p_H of 8 has been maintained in broth after autoclaving. CHEMICAL ABSTRACTS.

Extracellular Bacterial Proteases. K. G. DERNBY (*Biochem. Z.*, 1921, **126**, 105–108).—Bacteria were grown in a nutrient broth, then filtered through paper and a Chamberland candle. The sterile filtrate was examined for proteolytic activity by liquefaction of gelatin or hydrolysis of Witte's peptone. Tubercle bacilli, various pneumococci, various streptococci, staphylococci, and tetanus bacilli gave negative results. Active bacilli were *Bacillus subtilis*, *B. pyocyaneus*, *B. proteus*, *B. prodigiosus*, *B. sporogenes*, and *B. histolyticus*. These were active within the range p_H 4 to 9 with an optimum zone of 6 to 7. H. K.

Endo's Reaction, Biology of *Bacillus coli*. O. FERNÁNDEZ and T. GARMENDIA (*Anal. Fis. Quím.*, 1921, **19**, 313–319).—The red colour produced by *Bacillus coli* in Endo's medium (bouillon, with agar containing lactose, magenta, and sodium sulphite) is probably produced, not by acetaldehyde, but by lower acids of the fatty series. The production of acetaldehyde by the agency of *B. coli* was studied, using different modifications of Endo's medium and estimating the acetaldehyde produced by weighing its *p*-nitrophenylhydrazone. Increase in the amount of lactose or sodium sulphite and substitution of lactose and sodium sulphite by dextrose and sodium phosphate respectively did not result in

any marked increases in the amount of acetaldehyde produced. With mannitol and sodium sulphite, however, increased amounts of acetaldehyde were obtained. The maximum production of acetaldehyde was obtained, using a medium containing alanine, lactose, sodium chloride, and sodium sulphite. G. W. R.

Theory of Disinfection in the Light of the Meyer-Overton Lipoid Theory. P. G. F. VERMAST (*Biochem. Z.*, 1921, **125**, 106—148).—Experiments conducted with *Bacillus coli* show that in acid or neutral media disinfection with benzoic acid depends on the concentration of the undissociated acid. The benzoic acid anion and the hydrogen-ion concentration of the solution can undergo considerable variation without affecting the disinfection value, provided that the concentration of undissociated acid remains the same. The results with benzoic and salicylic acids confirm the Meyer-Overton theory in neutral and acid media if the distribution coefficient be based on the concentration of undissociated acid. In alkaline media, the disinfection value is not apparently in agreement with the theory. H. K.

Proteinogenous Amines. XII. The Production of Histamine and other Iminazoles from Histidine by the Action of Micro-organisms. MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1922, **50**, 131—191).—A study was made of the action of a large number of micro-organisms on histidine, using the standard medium previously employed (*A.*, 1919, i, 611). The results are presented in tabular form. In a few cases, evidence was obtained which suggested the rupture of the iminazole ring with the probable production of a triamino-carboxylic acid. Addition of leucine to the medium facilitated the growth of all the organisms, and, in those cases where decarboxylation occurred, increased the rate of production of histamine. The effect on *Bacillus coli cystitis* of additions of other amino-acids was also investigated. Alanine, leucine, arginine, glycine, and peptone augmented both the growth of the organism and the rate of production of histamine; tyrosine increased growth alone; glutamic acid and tryptophan increased growth, but diminished the yield of histamine; whilst cystine retarded growth and almost prevented the formation of histamine. E. S.

Pharmacology of Selenium and Tellurium. II. Action of their Acids on Diphtheria Bacilli. GEORG JOACHIMOWSKI and W. HIROSE (*Biochem. Z.*, 1921, **125**, 1—4).—The growth of diphtheria bacilli is inhibited by the oxy-acids of tellurium and selenium. The active concentrations of tellurium and selenium are, for tellurites 1 : 420, for tellurates 1 : 125, for selenites 1 : 1166, and for selenates 1 : 666. Diphtheria bacilli are much less sensitive than bacilli of the typhus-coli group, which latter are killed at dilutions of tellurium four hundred times the above. H. K.

Fermentation of *D*-Inositol. JAMES ARTHUR HEWITT and DOROTHY BEATTY STEABEN (*Biochem. J.*, 1921, **15**, 665—666).—The main products of the fermentation of inositol by *Bacillus*

lactis aerogenes are ethyl alcohol, acetic acid, succinic acid, and carbon dioxide, and small quantities of lactic acid and formic acid. Dextrose apparently is not an intermediate product.

W. O. K.

The Culture of *Bacillus pyocyaneus* on Definite Artificial Media. A. GORIS and A. LIOT (*Compt. rend.*, 1922, 174, 575-578; cf. *ibid.*, 1921, 172, 1622).—It has previously been shown that the ammonium salts of dibasic acids can serve as nutrients for *B. pyocyaneus*. It is now shown that the corresponding amides cannot serve as nutrients. Amino-acids may serve as nutrients for the bacillus provided that they have first been neutralised by sodium hydroxide, but, in general, they are less effective than the ammonium salts of the dibasic acids, particularly when they are used without the addition of mineral salts. The nutritive value of a given amino-acid depends, not only on the presence of one or more amino-groups, but also on the structure of the chain to which these groups are linked.

W. G.

The Production of Hydrocyanic Acid by *Bacillus pyocyaneus*. F. A. PATTY (*J. Infect. Dis.*, 1921, 29, 73-81).—The optimum reaction for the production of hydrogen cyanide by most strains of *B. pyocyaneus* is pH 5.4 to 5.8. The thiocyanate colorimetric method of estimating minute quantities of hydrogen cyanide is a satisfactory one, but control tests must be made, because in protein media there is sufficient thiocyanate formed on distillation to give a positive reaction. Oxygen is necessary for the production of hydrogen cyanide by *B. pyocyaneus*. Hydrogen cyanide is not produced by a filterable extra-cellular enzyme. Pigmentation, gelatin liquefaction, and hydrogen cyanide production, although independent functions, show a close relationship. Whole egg-broth is the most favourable medium for hydrogen cyanide production, but synthetic medium is second, indicating that a favourable synthetic medium may be devised. Contaminating organisms which do not produce hydrogen cyanide appear to be slightly inhibitive of its production. *B. pyocyaneus* does produce a measurable amount in the animal body. There is a marked variation among the different strains of *B. pyocyaneus* as regards the amount of hydrogen cyanide production.

CHEMICAL ABSTRACTS.

Trehalose Fermentation in the Differentiation of the Paratyphoid-enteritidis Group. S. A. KOSER (*J. Infect. Dis.*, 1921, 29, 67-72).—*Bacillus suispestifer* is unable to attack trehalose, whereas *B. paratyphosus*, *B. schottmulleri*, the animal para B subgroup, and *B. enteritidis* ferment it with the production of acid and gas. Furthermore, it is possible to differentiate by cultural methods the *B. schottmulleri* strains from the closely allied animal para B group, hitherto separable only by serological means. This has been accomplished by employing small amounts of a serum-water medium containing 0.5% trehalose and 1% Andrade indicator. In this medium, the animal para B strains produce a red coagulum after three to four days' incubation, whilst the *B. schottmulleri*

cultures present a light pink or colourless coagulum. This separation parallels the differentiation of these two groups by agglutinin absorption tests. *B. enteritidis* is similar in its reaction to the animal para B cultures and in contrast to *B. schottmulleri*.

CHEMICAL ABSTRACTS.

The Relation between Bacteria, Spores, and Formaldehyde.

E. HAILER (*Biochem. Z.*, 1921, **125**, 69—83).—Anthrax spores and vegetative bacterial forms, for example, paratyphus bacilli and staphylococci, were treated with formaldehyde solution followed by sodium sulphite solution. In the case of the spores, the sodium sulphite inhibits the toxic action of the formaldehyde the greater its concentration, provided that the formaldehyde has not been allowed to act too long. The results are interpreted on the theory that the formaldehyde forms an additive product with the amino-groups which is decomposed by sulphite, but prolonged action of formaldehyde gives rise to an irreversible complex, $-N=CH_2$. The results with bacteria are less simple.

H. K.

The Bactericidal After-effect of Formaldehyde Solutions.

E. HAILER (*Biochem. Z.*, 1921, **125**, 84—96).—The toxic action of formaldehyde continues after removal of anthrax spores or vegetative bacilli from the solutions if there be no nutrient material present. In the case of the spores, this after-effect is the more pronounced the drier the spores become, owing to loss of water and therefore increased formaldehyde concentration.

H. K.

Yeast Protein. ALEXANDER KIESEL (*Z. physiol. Chem.*, 1922, **118**, 304—306).—Yeast protein on hydrolysis yielded histidine 2.97%, arginine 3.15%, lysine 3.63%.

S. S. Z.

Stimulants of Alcoholic Sugar Fission. VIII.

CARL NEUBERG and MARTA SANDBERG (*Biochem. Z.*, 1921, **125**, 202—219).—Purines, their complex derivatives, or their degradation products accelerate the fermentation of dextrose by living yeast-cells just as they stimulate the action of press juice (this vol., i, 306). Caffeine and alloxan, however, retard the action of living yeast cells.

H. K.

Stimulants of Alcoholic Sugar Fission. IX.

CARL NEUBERG and MARTA SANDBERG (*Biochem. Z.*, 1921, **126**, 153—178).—With few exceptions, a large number of substances, belonging to very varied groups, have a stimulating influence on the action of living yeast and in some cases on press juice. The groups examined were, bitter substances, bile acids (sodium salts inhibit), various varieties of charcoal, saponins, cystin and its derivatives.

H. K.

Proteinogenous Amines. XIII. The Electronic Interpretation of certain Biochemical Phenomena.

MILTON I. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1922, **50**, 193—233).—Electronic formulæ for a number of organic compounds are deduced from their known chemical properties. From a consideration of these formulæ, the authors conclude that the decarb-

oxylation of pyruvic acid by yeast is a purely hydrolytic process, although no attempt is made to explain the mechanism of the action. Only those acids which contain quadruply positive carboxyl groups appear to be readily decarboxylated by yeast. Further, it is pointed out that, on the assumption that a quadruply negative carbon atom is only oxidised with difficulty, the behaviour of, at any rate, a number of acids in the animal body is readily explained by their electronic formulae. E. S.

Vitamins. II. Acceleration of Fermentation by Extracts of Animal Organs. SIGMUND FRÄNKEL and JOSEF HAGER (*Biochem. Z.*, 1921, **126**, 189—226).—The water-soluble extract of the alcoholic extract of a large number (31) of animal tissues was tested in its action on the evolution of carbon dioxide in yeast fermentation. All extracts except that of the bone marrow had a strong accelerating influence. H. K.

Vitamins. III. Acceleration of Fermentation by Extracts of Plants and the Action of Choline and Aminoethyl Alcohol on Fermentation. SIGMUND FRÄNKEL and ALBERT SCHARF (*Biochem. Z.*, 1921, **126**, 227—264).—The water-soluble portion of an alcoholic extract of a large number of grains and vegetables was examined in its action on yeast fermentation. Vegetable roots and grains were feebly active, leaves of vegetables were more active, but leek-like vegetables most active. Extract of celery and of yolk of eggs were very active, but both choline and aminoethyl alcohol were inhibitory. H. K.

Vitamins. IV. The Adsorption of Vitamins. SIGMUND FRÄNKEL and ALBERT SCHARF (*Biochem. Z.*, 1921, **126**, 265—268).—Using a purified water-soluble vitamin preparation from yeast (A., 1921, ii, 228), the authors have examined the adsorption of vitamin as determined by its accelerating influence on yeast fermentation, by Fuller's earth, kaolin, and alumina. Kaolin adsorbs it completely, Fuller's earth slightly less, and alumina not at all. H. K.

Vitamins. V. Further Experiments on the Chemistry of Vitamins. SIGMUND FRÄNKEL and ALBERT SCHARF (*Biochem. Z.*, 1921, **126**, 269—280; cf. A., 1921, ii, 228).—Further experiments are described on attempts to isolate the water-soluble vitamin from yeast and rice polishings. By examining the activity of preparations of vitamin on yeast fermentation, the vitamin was found in the mercuric chloride precipitate (choline fraction). In the case of rice polishings, the filtrate from the mercury precipitate was found inactive, the precipitate active but containing choline (isolated as platinum salt), which was inhibitory. From 2.5 kilos. of dry yeast, the choline fraction was freed from choline by precipitation as platinum salt and the active substance precipitated from the filtrate by aqueous mercuric chloride. A small yield of very active substance giving no carbohydrate reaction with Molisch's reagent was obtained. It contained N 4.75% (Pregl). H. K.

The Distribution of Urease in Plants. A. KIESEL and TROITZKI (*Z. physiol. Chem.*, 1922, **118**, 247—253).—Drying and autolysis diminish the urease activity of *Aspergillus niger*. This activity increases in the seeds and fruits of plants on ripening. Leaves contain more urease than stems and roots. On germination, the urease content increases, but the content of the enzyme diminishes again as the reserve material of the seeds is exhausted. S. S. Z.

The Invertase of *Mucor racemosus*. S. KOSTYTSCHEV and P. ELIASBERG (*Z. physiol. Chem.*, 1922, **118**, 233—235).—*Mucor racemosus*— contains, whilst *Mucor racemosus*+ does not contain, invertase. S. S. Z.

Enantiomorphism of Matter, Pasteur's Theory, and Life. S. CONDELLI (*Gazzetta*, 1921, **51**, ii, 309—324).—The author has subjected various racemic acids and amino-acids in nutrient solutions to the action of different bacteria and moulds. The results obtained are briefly as follows.

Both optically active malic acids are destroyed by the bacillus of fowl cholera, even at the ordinary temperature. With a solution containing the two enantiomorphous tartaric acids and dextrose, *Saccharomyces Pastorianus* II (Hansen) attacks only the sugar; doubt hence arises as to the affinity between the spacial configurations of an enzyme and the enantiomorph it preferably attacks. In the case of fermentations by yeasts in acid media, the influence of the acid appears to be solely due to the acidity it produces. Results similar to those obtained with the bacillus of fowl cholera are given by *Bacillus Fitzianus* in presence of a racemate. In the action of various schizomycetes on glyceric acid, the degree to which one of the two enantiomorphs is selected in preference to the other varies with the different organisms from a minimum to a maximum, the pure lævorotatory acid being left when *B. Fitzianus* is employed; these results confirm that of Frankland and Frew (T., 1891, **59**, 96) and not that of Lewkowitsch (A., 1883, 1124).

Penicillium glaucum acts on the sweet dextrorotatory asparagine in preference to the natural insipid lævorotatory enantiomorph. The bacillus of fowl cholera attacks lævorotatory in preference to the dextrorotatory aspartic acid, although the latter is derivable from *d*-asparagine; the acid function appears to influence the choice in this case. With tyrosine, two different moulds exhibit slight selection, in one case for the one and in the other for the other isomeride; tyrosine is not attacked by the bacillus of fowl cholera. *P. glaucum* acts on *l*-leucine more rapidly than on the dextro-isomeride (cf. Schulze and Bosshard, *Z. physiol. Chem.*, 1892, **9**, 100).

The author contests the view that asymmetry is a characteristic of life. T. H. P.

The Physiology of the "Polyamyloses." I. HANS PRINGSHEIM and KARL O. MÜLLER (*Z. physiol. Chem.*, 1922, **118**, 236—240).—*Spirogyra dubia* which was previously freed from starch

was allowed to act on various substances with the purpose of ascertaining whether starch could be formed from them. Glycerol, dextrose, lævulose, galactose, maltose, and cellobiose gave positive results. No starch was formed from the "polyamyloses."

S. S. Z.

An Indicatory Method for Evaluating the Vitality of Seeds by a Biochemical Method. ANTONIN NĚMEC and FRANTIŠEK DUCHOŇ (*Compt. rend.*, 1922, **174**, 632—634; cf. this vol., i, 94).—The catalase activity of the seed is measured by determining the amount of oxygen liberated under definite conditions from hydrogen peroxide by a known weight of the seed previously ground to powder. Results with numerous different species show that the volume of oxygen liberated increases steadily with the germinative capacity of the seed, the curve showing their relationship being a smooth one.

W. G.

The Alleged Development of Hydrogen Peroxide in Carbon Dioxide Assimilation. HANS MOLISCH (*Biochem. Z.*, 1921, **125**, 257—261).—The author was unable to confirm the production of hydrogen peroxide in the assimilation of carbon dioxide by plants as described by Kleinstück (*A.*, 1918, ii, 107). H. K.

Energy Exchange in Carbon Assimilation by Green Cells. C. MÜLLER and O. WARBURG (*Ber. Physikal.-Techn. Reichsanst.*, 1920; from *Chem. Zentr.*, 1921, iii, 1205).—The utilisation of energy in the assimilation of carbon by *Chlorella vulgaris* in a nutrient solution saturated with 4% of carbon dioxide was studied for different wave-lengths. The percentage utilisation of energy in different parts of the spectrum was as follows: red (600—710 μ) 14%; yellowish-red (600—650 μ) 20%; orange (570—610 μ) 23%; yellow (550—590 μ) 21%; green (510—550 μ) 15%; blue (445—500 μ) 13%.

G. W. R.

Hydrogen-ion Concentration of Plant Cells. W. R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1922, **16**, 414—434).—A summary is given of earlier work on the reaction of plant cells and of the experimental methods used. Observations are recorded of the hydrogen-ion concentrations of a large number of plants. Varying reactions are found under differing cultural conditions and in different parts of the same plant. The values recorded range from P_H 1.4 to P_H 8. The P_H value in any tissue is generally near to but rather less than the optimum for the characteristic enzyme at ordinary temperatures, which ensures that the enzyme is not destroyed at higher temperatures which may be experienced. Diethyl-red is recommended as a reagent for microchemical work.

G. W. R.

The Variation in the Manganese Content of Leaves with Age. GABRIEL BERTRAND and (MME) M. ROSENBLATT (*Compt. rend.*, 1922, **174**, 491—493; cf. *A.*, 1921, i, 759; Jadin and Astruc, *A.*, 1913, i, 948).—The plants examined may be divided into four groups according to the manner of the variation of the manganese

content of their leaves with age, but there are certain species which fall between two groups. In the first two groups, the manganese content of the leaves is at a maximum at the commencement of the leaf formation and then diminishes with age, the rate of diminution differing with the group. In the third group, the manganese content increases very rapidly with age to a maximum and then diminishes. In the fourth group, the manganese content increases continuously with age. W. G.

Action of Soluble Lead Salts on Plants. EUGÈNE BONNET (*Compt. rend.*, 1922, 174, 488—491).—Lead salts exert an unfavourable influence on the growth of plants, their effect being most marked in the curtailment of root development and to some extent of stem development. The plants absorb lead and the metal is found entirely in the roots. W. G.

The Presence of Ornithine in Plants. ALEXANDER KIESEL (*Z. physiol. Chem.*, 1922, 118, 254—266).—So far, experiments to prove the presence of ornithine in plants have yielded negative results; it appeared possible that this might be due to the reagents employed. Experiments on the precipitation of ornithine by phosphotungstic acid, silicotungstic acid, tungstic acid, phosphomolybdic acid, Staněk's reagents, potassium bismuth iodide, potassium mercury iodide, and cadmium chloride show that they would fail to precipitate the small amounts of ornithine likely to be present in plant extracts. S. S. Z.

The Glutencasein of Buckwheat. ALEXANDER KIESEL (*Z. physiol. Chem.*, 1922, 118, 301—303).—The glutencasein of buckwheat was found to yield on hydrolysis histidine 0.84%, arginine 7.13%, and lysine 1.48%. S. S. Z.

***Digitalis purpurea* Growing Wild on the Uplands of Desulo (Sardinia).** R. BINAGHI (*Gazzetta*, 1921, 51, ii, 284—288).—The *Digitalis purpurea* growing wild at Desulo contains sufficient digitoxin to render it of medicinal value. The best method of extraction on a large scale is that given by Nativelle (A., 1875, 276), and Fromme's modification of Keller's method serves well for the rapid estimation of the content of digitoxin. T. H. P.

The Formation of Anthocyanin Pigments. RAOUL COMBES (*Compt. rend.*, 1922, 174, 240—242; cf. A., 1909, ii, 420).—A reply to Jonesco (this vol., i, 97), in which the author considers that the materials taken by Jonesco for γ -pyrone pigments were only tannins and that, in consequence, his conclusions were false. W. G.

The Hydrocyanic Acid Question. VII. *Cornus sanguinea*. L. ROSENTHALER (*Schweitz. Apoth. Zeit.*, 1921, 59, 465—469; from *Chem. Zentr.*, 1921, iii, 1247).—The leaves of *Cornus sanguinea*, L., do not contain hydrocyanic acid. The very rare occurrence of hydrocyanic acid and saponin together in the same plant suggests that there is no correlation between the occurrence of these substances. G. W. R.

Variations in the Chemical Composition of Fucaceæ. L. LAPIQUE and L. EMERIQUE (*Compt. rend. soc. biol.*, 1921, **85**, 172—175; from *Physiol. Abstr.*, 1922, **6**, 645).—The composition of Laminaræ shows an annual periodicity, the carbohydrate increasing in the summer and the ash constituents decreasing. *Fucus serratus* is similar, except that in June it contains a large quantity of mineral matter. *F. vesiculosus* exhibits a minimum of soluble ash constituents in June. *F. platycarpus* has a higher ash content. The analytical results are tabulated. E. S.

Western Sneezeweed (*Helenium hoopesii*) as a Poisonous Plant. C. DWIGHT MARSH, A. B. CLAWSON, JAMES F. COUCH, and HADLEIGH MARSH (*U.S. Dept. Agr. Bull.*, 1921, No. **947**, 1—46).—*H. hoopesii* contains a glucoside, *dugaldin*, which is poisonous to cattle. Dugaldin is a bitter, white, amorphous solid which forms a sparingly soluble, relatively slightly toxic compound with tannic acid. Helenic acid, the active principle of *H. autumnale*, does not occur in *H. hoopesii*, nor do alkaloids, toxic saponins, or hydrogen cyanide. CHEMICAL ABSTRACTS.

The Colouring Matter of the Scarlet Pelargonium. GEOFFREY SAUNDERS CURREY (*T.*, 1922, **121**, 319—323).

Lignin as it Occurs in Wood. PETER KLASON (*Ber.*, 1922, **55**, [B], 435—456).—Fagerlind and Klason (*Schriften Vereins Zellstoff. Papier Chemiker*, 2) have described the isolation of lignin from pine wood by repeated alternate extractions of the wood with boiling water and alcohol containing a small quantity of acetic acid. Re-examination of the product proves that it contains water which had been overlooked and, after the necessary corrections thus involved the analytical data are found to agree excellently with those calculated for lignin (A., 1920, i, 821). The substance gives the usual lignin reactions. As far as can be observed by reason of the colour of the solutions, lignin and lignosulphonic acid are optically inactive. H. W.

The Colouring Matter of Red Roses. GEOFFREY CURREY (*Proc. Roy. Soc.*, 1922, [B], **93**, 194—197).—An examination of the petals of the deep red rose "George Dickson" has shown the presence of the anthocyanin pigment cyanin (A., 1915, i, 282) to the extent of 10% of the dried petals. An unidentified yellow sap pigment is also present. It yields an anthocyanin on reduction. H. K.

The Enzymic Degradation of Arginine in Plants. II. ALEXANDER KIESEL (*Z. physiol. Chem.*, 1922, **118**, 267—276).—The presence of arginase has been established in ergot (*Secale cornutum*) and in *Vicia sativa* by demonstrating the formation of ornithine from arginine. Ammonia was also formed in the reaction. Traces of ornithine are evidently also produced by *Angelica silvestris* and *Trifolium pratense*. S. S. Z.

The Action of Arginase on Agmatine and Tetramethyldiguanidine. The Specificity of Enzymes. ALEXANDER KIESEL (*Z. physiol. Chem.*, 1922, **118**, 284—300).—The action of

Aspergillus niger, *Secale cornutum*, *Agaricus campestris*, *Vicia sativa*, *Lupinus albus* and *Trifolium pratense* on agmatine and tetramethylenediguanidine has been studied. Agmatine is not decomposed by these organisms, whilst tetramethylenediguanidine is only acted on by *Aspergillus niger* with the formation of agmatine. S. S. Z.

The Tryptophan Content of Important Foodstuffs. TOSMIDE (*Z. expt. Med.*, 1921, **24**, 166—207).—The tryptophan content of cereals was estimated indirectly from that of the three seed components (sodium chloride-soluble protein, alkali-soluble protein, and alcohol-soluble protein), Fürth and Nobel's method being employed. The figure for maize is about half that for wheat, rye, barley, oats, and rice, but great individual variations were observed. In the case of legumes, a 10% sodium chloride extract of the proteins of the different flours yielded relatively high results (more than 0.5%) which were unaffected by removal of the germ. The direct method showed that raw white of egg protein contains 2.56%, and dried white of egg 3.18%, greater hydrolysis taking place when the latter is dissolved, whilst raw and dried yolk both contain about 2.45%. Cow's milk gave results between 0.068 and 0.094%, whereas human milk yields a higher figure. The proteins of cheese contain 2.48% of tryptophan; of unsweetened condensed milk, 2.28%; of sweetened condensed milk, 2.35%; and of dried milk, 2.71%.

CHEMICAL ABSTRACTS.

The Chemical Composition of Maize Oil. WALTER F. BAUGHMAN and GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1921, **43**, 2696—2702).—The sample of maize oil examined had d_4^{20} 0.9185; n_D^{20} 1.4717; iodine number (Hanus), 117.2; saponification number, 187.3; unsaponifiable matter, 1.7%; saturated acids, 11.2%; unsaturated acids, 82.5%. Detailed analysis showed its composition to be as follows: Glycerides of oleic acid 45.4%, of linoleic acid 40.9%, of palmitic acid 7.7%, of stearic acid 3.5%, of arachidic acid 0.4%, of lignoceric acid 0.2%, and 1.7% of unsaponifiable matter, total 99.8%. There was no evidence of the presence of any hypogæic acid (cf. Leathes, "The Fats," 1910). W. G.

Nitrogen Compounds in Lucerne Hay. HARRY G. MILLER (*J. Amer. Chem. Soc.*, 1921, **43**, 2656—2663).—Non-protein nitrogenous compounds to the extent of about 28% of the total nitrogen were easily extracted with hot water from lucerne hay regardless of the fineness of the hay. Alkali hydroxides extracted more protein from the finely ground than from the coarse material. Such protein extracted by dilute alkali had a nitrogen content of 13.0% and contained the basic amino-acids arginine, histidine, lysine, and cystine. As compared with the seed (cf. A., 1921, i, 486), the leaf protein contained smaller amounts of arginine and amide nitrogen and this may account for the difference in the total nitrogen of the two proteins.

The purine fraction contained 3.2% of the total nitrogen, and a

crystalline salt corresponding with the hypoxanthine silver salt was isolated. W. G.

The Manganese Content of Potatoes. G. BODE and K. HEMBD (*Biochem. Z.*, 1921, 124, 84—89).—The manganese content of twenty varieties of potatoes grown without addition of fertilisers containing manganese was determined colorimetrically as permanganate by Marshall's method (A., 1901, ii, 350) and simultaneously the silica and phosphate content. The mean manganese content of 1.4 mg. per 100 grams of dried material does not show any extreme variations. There is no parallelism between the manganese content and the silica or phosphate content or with the content of protein or starch, the melanin number, or yield of tubers. H. K.

Composition of Wild Beetroots. E. SAILLARD (*Compt. rend.*, 1922, 174, 411—412).—The wild beetroots from Finistère which were analysed were found to contain higher percentages of dry matter, insoluble marc, total nitrogen, mineral matter, chlorine, sodium, magnesium, and phosphoric acid than the cultivated varieties. Their sugar content varied from 14 to 20%, but their juice, as a source of sugar, was rather impure. W. G.

Progressive Disappearance of Free Sulphurous Acid in a Preserved Apple Juice. WARCOLLIER and LE MOAL (*Compt. rend.*, 1922, 174, 634—637).—The sulphited juices examined were made from rotten apples, and the conversion of free added sulphurous acid into combined acid was investigated. It was found to be due to the action of oxidising enzymes present in the moulds of the juice. These enzymes formed, at the expense of the sugars and pectins of the juice, substances having aldehydic or ketonic structure, which fixed the sulphurous acid. At the same time, there was a marked increase in the acidity of the medium. Such juices should not, in consequence, be used for preserving and sweetening cider. W. G.

Copper Sprays. G. VILLEDIEU and (MME) G. VILLEDIEU (*Compt. rend.*, 1922, 174, 707—709; cf. A., 1920, i, 704).—It has previously been shown that the traces of copper which can be dissolved by the rain from the deposits on the leaves of plants could not prevent the germination of the zoospores of mildew. It is now shown that a 2% solution of sodium sulphate or a 1.5% solution of sodium or potassium chloride completely prevents the bursting of the conidia of phytophthora. A similar result is obtained by using a saturated solution of calcium sulphate. The authors consider that the anticryptogamic power of copper sprays may be explained as due to the presence of these alkali or calcium salts, without considering the possible conversion of the copper into a soluble form. W. G.

Relation of the Hydrogen-ion Concentration of the Soil to Plant Distribution. W. R. G. ATKINS (*Nature*, 1921, 108, 80—81; cf. following abstract).—Wherry's (*Proc. Acad. Nat. Sci. Philadelphia*, 1920, 113) observation that the distribution of a

species is closely related to the p_H of the soil, has been tested and found applicable to the distribution of a number of plants in India and the British Isles, the limiting p_H values being given in each case. Although plants may survive, or even thrive, in cultivation outside their normal limits, yet in free competition with their neighbours, a sufficiently great divergence from the normal p_H value for the species is always a deciding factor. A. A. E.

Relation of the Hydrogen-ion Concentration of the Soil to Plant Distribution. NORMAN M. COMBER (*Nature*, 1921, 108, 146—147; cf. preceding abstract).—In view of the fact that some plants which are usually very susceptible to acidity will thrive in certain soils of p_H 4—5, and will show no response to liming, it is inferred that the effect of the hydrogen-ion concentration of the soil on plants is indirect, and that there is some ulterior factor, the fluctuations of which are commonly, but not invariably, accompanied by fluctuations of hydrogen-ion concentration. For instance, in mineral soils variations in the concentrations of certain multivalent ions, particularly aluminium ions, will roughly correspond with variations in the hydrogen-ion concentration. A. A. E.

Chemistry of the Oxidation of Sulphur to Sulphuric Acid by Micro-organisms, and Transformation of Insoluble Phosphates into Soluble Forms. SELMAN A. WAKSMAN and JACOB S. JOFFE (*J. Biol. Chem.*, 1922, 50, 35—45).—The sulphuric acid produced in the soil by sulphur oxidising bacteria converts insoluble into soluble phosphates (cf. Lipman, McLean, and Lint, A., 1916, i, 784). Using cultures of the organism in a liquid medium to which tricalcium phosphate has been added, it is shown that the acidity of the medium increases to about P_H 2.8, at which value it remains constant until all the phosphate has been converted into a soluble form. E. S.

Practical Significance of the Organic Carbon : Nitrogen Ratio in Soils. J. W. READ (*Soil Sci.*, 1921, 12, 491—495).—The results of analyses are recorded showing the carbon : nitrogen ratio and crop yields of a number of soils. In general, the lower ratios are associated with low percentages of organic matter, but no correlation between the ratio and crop yields is apparent. A. G. P.

Nitrification in Acid Soils. R. E. STEPHENSON (*Iowa Expt. Sta., Research Bull.*, 1920, 58, 331—349).—Nitrification may take place in acid soils. The addition of lime produced no measurable effect on the nitrification of the original soil nitrogen, but it caused a marked increase in the nitrification of ammonium sulphate added to the soil. Although very large amounts of lime may increase the nitrifying power of a soil, only that necessary to neutralise the most active acids (as shown by an estimation of the lime requirement) is essential for adequate nitrification and maximum crop production. CHEMICAL ABSTRACTS.

Organic Chemistry.

Natural System of Carbon Compounds. I. General Statement of MendeléeV's Law on the Numerical Relationships between Primary, Tertiary, and Quaternary Carbon Atoms. HERMAN DECKER (*Helv. Chim. Acta*, 1922, 5, 201—205).—If qu represents the number of quaternary, te that of the tertiary, and pr that of the primary carbon atoms in the hydrocarbon C_nH_{2n+p} , $pr-p=2qu+te$, or the relation between pr , te , and qu in every homologous series is determined by the series-constant p . For compounds composed entirely of benzene nuclei, the expression becomes $-p=2qu+te$. If the number of the nuclei be R^{ar} , $R^{ar}=qu/2+1$, or the number of nuclei exceeds by one the number of quaternary carbon atoms. J. K.

The Action of Nitrosyl Chloride on Normal Heptane. E. V. LYNN and O. HILTON (*J. Amer. Chem. Soc.*, 1922, 44, 645—648).—In confirmation of previous work (A., 1919, i, 245), it is shown that nitrosyl chloride reacts with normal heptane in sunlight, giving di-*n*-propylnitrosomethane, which suffers rearrangement with formation of dipropyl ketoxime. When distilled with steam, the oxime decomposes, giving the ketone and hydroxylamine. W. G.

A New Heptane: Trimethylisopropylmethane [$\beta\beta\gamma$ -Trimethylbutane]. G. CHAVANNE and B. LEJEUNE (*Bull. Soc. chim. Belg.*, 1922, 31, 98—102).— $\beta\beta\gamma$ -Trimethylbutane is prepared from pinacolin by the action of magnesium methyl iodide. The additive compound is decomposed by dilute acetic acid, yielding pentamethylethanol [$\beta\gamma\gamma$ -trimethylbutan- β -ol] (cf. Henry, A., 1906, i, 477). This, on dehydration with *p*-toluenesulphonic acid, is converted into a heptylene, $\beta\gamma\gamma$ -trimethyl- Δ^c -butylene, CM_2CMeCH_2 , which, when treated in acetic acid solution with hydrogen in presence of platinum black, yields the heptane, a liquid of camphor-like odour, b. p. 80.75°/760 mm., m. p. -25° , d_4^{20} 0.6945, d_4^{25} 0.7065, n_D^{20} 1.3903, n_D^{25} 1.3923, n_B^{20} 1.3971, n_D^{25} 1.4008. The following constants were determined for the heptylene: d_4^{20} 0.7101, d_4^{25} 0.7235, n_D^{20} 1.4032, n_D^{25} 1.4059, n_B^{20} 1.4119, n_D^{25} 1.4164. H. J. E.

The Influence of the Elements of the Oxygen Group on Paraffin Wax. H. SIEBENECK (*Petroleum*, 1922, 18, 281—286).—Paraffin wax is fairly readily attacked by air or oxygen if the gas is bubbled through the material heated at about 135°. After ten hours, acid vapours are evolved, and after twenty-two hours the product remaining contains from 30—40% of saponifiable substances, according to whether pure oxygen or air is used. By continuing the experiment, a product containing 52.65% of saponi-

fiable substances was obtained having an acid value 59.03 and an ester value 93.91, corresponding with about 30% of free and 70% of esterified acids. The acids belong to the acetic acid series, lower members of which series are also present in the volatile portion of the product of oxidation together with water, amounting in all to about 7% of the paraffin employed. When paraffin wax is heated with sulphur, evolution of hydrogen sulphide commences at 150°, and at 230° this gas is liberated freely together with carbon disulphide. After seventy-two hours' treatment at this temperature, a brownish-black, fatty mass remained, from which, after extraction with carbon disulphide and then with ether, an amorphous, black substance was isolated containing only a negligible percentage of hydrogen and having a composition agreeing closely with the formula $(C_5S)_x$. The substance is indifferent to alkalis and organic solvents, but is attacked by concentrated sulphuric and nitric acids. Similar dehydrogenation of the paraffin was observed under the action of selenium and tellurium, but higher temperatures (300–370°) were necessary, and no product corresponding with the sulphurised paraffin could be isolated. The presence of small quantities of sulphur or selenium apparently completely inhibited the action of oxygen on the paraffin.

G. F. M.

Chemical Reactions Induced by the Silent Discharge. I. Ethylene and Nitrogen. II. Benzene and Carbon Dioxide. SUSUMU MIYAMOTO (*J. Chem. Soc. Japan*, 1922, **43**, 21–48).—

I. A mixture of 1 volume of ethylene and 2 volumes of nitrogen was submitted to the electric field given by an alternating current of 10,000 volts and 50 cycles, in an apparatus cooled with water. The following substances were isolated: (1) A nitrile, $C_{18}H_{31}CN$, a light yellow liquid having a stimulating odour, b. p. 82–85°/10 mm., the hydrolysis of which gave an oily acid, $C_{18}H_{31}CO_2H$, and a silver salt, $C_{18}H_{31}CO_2Ag$, a yellow precipitate, m. p. 160° (approx., decomp.). (2) An amine, $C_{20}H_{38}N_4O_2$, which formed the following salts: *platinichloride*, yellow crystals, darkening at about 150°, *aurichloride*, yellow crystals, darkening at about 180°; *picrate*, yellow crystals, melting and darkening at about 170°. (3) The substances $C_{11}H_{20}O$, b. p. 58–65°/11 mm.; $C_{12}H_{22}O$, b. p. 73–79°/11 mm.; $C_{13}H_{24}O$, b. p. 87–93°/11 mm.; a mixture of $C_{14}H_{26}O$ and $C_{15}H_{28}O_2$, b. p. 97–103°/11 mm.; and $C_{18}H_{34}O$, b. p. 112–115°/11 mm.; these are presumed to be produced by the oxidising action of air on the unsaturated hydrocarbons, $C_{10}H_{20}$, $C_{12}H_{22}$, $C_{13}H_{24}$, $C_{15}H_{26}$, and $C_{18}H_{34}$, respectively, formed initially. (4) A substance, $(C_{22}H_{34}O_2)_n$, a yellow powder, which does not decompose at 300°, (5) hydrogen cyanide, (6) acetylene, (7) hydrogen, and (8) ethane; the last two gases and a compound, $C_{16}H_{32}N_4$, have been isolated by Berthelot in the same reaction (A., 1899, i, 657).

II. When a mixture of carbon dioxide and benzene vapour was passed through the apparatus under like conditions, the phenol, $(C_{10}H_{10}O_2)_3$, a yellow powder, decomposing and darkening at about 100°, was isolated.

K. K.

Photochemical Studies. XIII. Photopolymerisation of Vinyl Chloride and the Problem of Caoutchouc. JOH. PLOTNIKOW (*Z. wiss. Photochem.*, 1922, **21**, 117—134; cf. A., 1921, ii, 146).—Solutions of vinyl chloride in 99% ethyl alcohol, acetone, carbon disulphide, benzene, methyl alcohol, ethyl ether, toluene, and carbon tetrachloride have been subjected to ultra-violet light for periods of six hours at temperatures between 25.2° and 15.2°. In all solvents except benzene and carbon disulphide, a polymerisation occurs easily when the extreme ultra-violet is used, and a white, amorphous compound separates. In the case of carbon disulphide, there is no action, and with benzene an oily product is formed. In the normal action, the chlorine atom acts as an internal catalyst. The process has a temperature coefficient 1.03. Of all the solvents employed, methyl alcohol and ethyl alcohol are the most suitable. Salts of manganese, cobalt, nickel, copper, and vanadium act catalytically in the sense that they cause the reaction to take place in visible light. Carbon tetrachloride accelerates the reaction in ultra-violet light. Uranyl salts are the strongest catalysts, and a process for the preparation of the product by the action of sunlight in the presence of uranyl salts has been worked out and will be published later in the patent literature. The product of the reaction is described as a pure white, light powder resembling rice powder, which is slightly soluble in acetone, methyl alcohol, and ethyl alcohol, more soluble in benzene, chlorobenzene, carbon tetrachloride, and carbon disulphide, and very soluble in phenyl acetate. It separates from the solvents, in which it is fairly soluble, as an elastic film which loses its elasticity on keeping. By suitably mixing with vaselin, aniline, balsam of Peru, and similar substances, waxes, jellies, and solid elastic masses may be obtained.

J. F. S.

The System Water-Ethyl Alcohol-Carbon Disulphide. Miscibility of the Three Components in Different Proportions and some Practical Applications. N. SCHOORL and (Mlle) A. REGENBOGEN (*Rec. trav. chim.*, 1922, **41**, 125—134).—The diagram is given of the ternary system showing the limits of homogeneous mixtures at temperatures of 0°, 10°, 20°, 40°, 60°, and 80°, also diagrams for binary mixtures of ethyl alcohol and carbon disulphide showing critical temperatures at which separation takes place. The results are applicable to the estimation of the water content of alcohol, especially for high percentages of the latter, by the determination of the temperature of homogeneous mixing of two volumes of the alcohol with five volumes of carbon disulphide.

H. J. E.

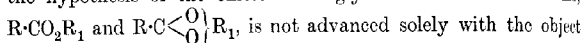
The Composition of the Residue on Distillation of Crude Glycerin. E. LEWIS (*J. Soc. Chem. Ind.*, 1922, **41**, 97—100r).—An average sample of glycerin residues contained 19.56% of diglycerol (or polyglycerols). The polymerised glycerols are produced from glycerol under the influence of heat and pressure, and their formation is accelerated by the presence of alkaline salts, and by such catalysts as iodine and bromine. No simple means was found

for depolymerising these substances and recovering the glycerol, as even when a certain amount of depolymerisation was effected by means of high pressures at various temperatures further polymerisation occurred on distilling the mixture owing to the salts present. In addition, a considerable proportion of the depolymerised product was converted during the process into glyceric acid, glyceraldehyde, and a hexose sugar. Pure diglycerol was prepared by heating glycerol for two hours at 210° with 0.05% of iodine. On distillation in a vacuum, an 85% yield of a water-white, viscous, and very hygroscopic fluid, b. p. $257-260^{\circ}/30$ mm., $d_{20}^{20}=1.3215$, $d_{40}^{20}=1.3183$, was obtained.

During the investigation, the b. p. of anhydrous and aqueous solutions of glycerol were determined at 760 mm. pressure, the following being selected from the results recorded: 100% glycerol 290° , 99% 225.3° , 98% 196.0° , 95% 160° , 90% 137.5° , 80% 121.5° , 50% 106.0° , 10% 101.0° . The specific gravities of mixtures of glycerol with diglycerol, and with water in various proportions, were also determined and the results are recorded in tabular form.

G. F. M.

The Constitution of Glycerides from the Point of View of the Co-ordination Theory. AD. GRÜN (*Oesterr. Chem. Ztg.*, 1922, **25**, 37-38).—In reply to Klimont, it is pointed out that the hypothesis of the existence of glycerides in the two forms,



is not advanced solely with the object of explaining the double melting point of certain glycerides, but mainly to account for their unusual reactivity, which frequently resembles that of salts except in the greater slowness of reaction. Reasons are advanced for considering the isolation of co-ordination forms less probable in the cases of methyl and ethyl esters than of glycerides. The author does not consider that dimorphism adequately explains the occurrence of glycerides in forms with different melting points, and regards the dimorphism as the outward expression of difference in internal structure.

H. W.

Production and Reactions of $\beta\beta'$ -Dichlorodiethyl Sulphide. FREDERICK GEORGE MANN and WILLIAM JACKSON POPE (*T.*, 1922, **121**, 594-603).

Preparation of Esters of Dihydroxydiethyl Sulphide. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (*Brit. Pat.* 154907).—The esters are obtained by the interaction of organic acids or their anhydrides and dihydroxydiethyl sulphide. Thus, *diacetoxydiethyl sulphide* is prepared by slowly dropping 5 parts of dihydroxydiethyl sulphide on to 6 parts of acetic anhydride heated at 120° . It is a stable, mobile liquid, b. p. $142-150^{\circ}/12$ mm. The corresponding diformyl compound boils at $130-137^{\circ}/7$ mm.

G. F. M.

Sesqui-mustard Gas or Bis- β -chloroethyl Ether of Ethylene Dithioglycol. RAPHAEL ROSEN and E. EMMET REID (*J. Amer. Chem. Soc.*, 1922, **44**, 634-636).—The work recorded is

in complete agreement with that of Bennett (T., 1921, **119**, 418, 1860), except in so far as the melting point of ethylene bis- β -hydroxyethyl sulphide is concerned. In a footnote the authors state that their product was probably impure. W. G.

A Homologue of Ethylene Sulphide: Trimethylethylene [β -Methyl- Δ^2 -butylene] Sulphide. G. CALLINGAERT (*Bull. Soc. chim. Belg.*, 1922, **31**, 109—111; cf. Delépine, A., 1920, i, 526; 1921, i, 156).— β -Methyl- Δ^2 -butylene dibromide is transformed into the corresponding dithiocyanate and this is shaken in the cold with sodium sulphide solution, the product being distilled with steam. β -Methyl- Δ^2 -butylene sulphide so obtained is a mobile, colourless liquid, b. p. 145—150°, d_4^{20} 0.927. H. J. E.

The Action of Selenium Monochloride on Propylene, Butylene, and Amylene. C. E. BOORD and F. F. COPE (*J. Amer. Chem. Soc.*, 1922, **44**, 395—401).—The action between ethylene and selenium monochloride resulting in the formation of $\beta\beta'$ -dichlorodiethyl selenide dichloride (cf. Bauser, Gibson, and Pope, T., 1920, **117**, 1453) really takes place in two stages: $2C_2H_4 + Se_2Cl_2 = (C_2H_4Cl)_2Se + Se$; and $(C_2H_4Cl)_2Se + Se_2Cl_2 = (C_2H_4Cl)_2SeCl_2 + 2Se$. The action may be stopped at the first stage by adding the selenium monochloride to the ethylene. These two stages have been obtained with propylene, butylene, and amylenes, but with the last two it is not easy to complete the second stage. The compounds described are $\beta\beta'$ -dichlorodipropyl selenide, b. p. 134°/10 mm., and its dichloride, m. p. 81°; $\beta\beta'$ -dichlorodibutyl selenide, b. p. 138°/8 mm., and its dichloride; $\beta\beta'$ -dichlorodiamyl selenide, b. p. 158°/10 mm., and its dichloride. These results are taken as further evidence in favour of the unsymmetrical structure, $SeSeCl_2$, for selenium monochloride. W. G.

Action of Carbon Disulphide on Mercuric Acetate. A. BERNARDI and G. ROSSI (*Gazzetta*, 1922, **52**, i, 139—140).—The action of carbon disulphide on cold, saturated mercuric acetate solution, even in the dark, proceeds according to the equation: $CS_2 + 2(CH_3CO_2)_2Hg + H_2O = S(HgCO_2CH_3)_2 + COS + 2CH_3CO_2H$. The compound, $S(HgCO_2CH_3)_2$, forms a crust of white, silky needles, begins to decompose without melting at 215°, appears to be insoluble in all solvents, is decomposed by hot mineral acids, and yields mercuric sulphide when treated with either water or sodium thiosulphate. T. H. P.

Mangani-acetates and -benzoates. R. F. WEINLAND and GEORG FISCHER (*Z. anorg. Chem.*, 1921, **120**, 161—180).—Complex salts derived from ferric and chromic acetates have been described, particularly those containing pyridine in the complex kation, for example, $[Cr(OAc)_6Py_3(OH)_2]H_3$ (A., 1910, i, 503) and $[Fe(OAc)_6Py_3O]Cl_4$ (A., 1913, i, 644). Derivatives of manganic acetate have now been prepared containing pyridine in the complex kation. These are more nearly related to the iron than to the chromium compounds, and appear to contain four atoms of

metal in the inner complex. They are generally brown in colour, are decomposed by water, and are soluble in alcohol.

Perchlorates. $[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})_2](\text{OAc})_3\text{ClO}_4$, long, narrow, rectangular tablets; $[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})_3](\text{OAc})_2\text{ClO}_4$, well-formed, long, thin tablets, also crystallises with $2\text{H}_2\text{O}$;

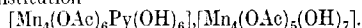
$[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})_4](\text{OAc})\text{ClO}_4\cdot 2\text{H}_2\text{O}$, aggregates of thin needles; $[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})_3](\text{OAc})_{1.5}(\text{ClO}_4)_{1.5}$, thin needles which recrystallise unchanged from alcohol.

Nitrates. $[\text{Mn}_4(\text{OAc})_6\text{Py}_4](\text{OAc})_4(\text{NO}_3)_2$, thin, rectangular needles; $[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})](\text{OAc})_{3.5}(\text{NO}_3)_{1.5}$, oblique tables; $[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})_2](\text{OAc})_2(\text{NO}_3)_2 +$

$2[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})](\text{OAc})_4\cdot \text{NO}_3$ very thin, long, rectangular tables, and

$[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})_2](\text{OAc})_{2.5}(\text{NO}_3)_{1.5}$, very thin, rectangular tables.

Acetates. $[\text{Mn}_4(\text{OAc})_6\text{Py}_5\text{O}_2](\text{OAc})_2$, lustrous, octahedral crystals from a solution of manganic acetate in pyridine; recrystallised from alcohol, it gives $[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})_4](\text{OAc})_2$, of similar crystalline form; a more complex compound crystallising in brownish-black columns with a well-marked cleavage appears to have the constitution



Other more complex nitrates and perchlorates of doubtful constitution were also obtained. Red manganic acetate probably has the constitution $[\text{Mn}_3(\text{OAc})_6(\text{H}_2\text{O})_2](\text{OAc})_3\cdot 4\text{H}_2\text{O}$.

A new manganic benzoate with alcohol of crystallisation was prepared, $[\text{Mn}_3(\text{OBz})_6(\text{OH})_3\text{EtOH}]$, large, red crystals. Two pyridine compounds were isolated, both apparently containing a tetramanganikation: $[\text{Mn}_4(\text{OBz})_6(\text{OH})_3\text{Py}_2]\text{OBz}$, and



The Action of Alumina, Titania, and Thoria on Ethyl and isoPropyl Acetates. HOMER ADKINS and A. C. KRAUSE (*J. Amer. Chem. Soc.*, 1922, **44**, 385—392).—Contrary to a statement of Sabatier, it is shown that alumina, titania, and thoria are not specific in so far as the mode of decomposition of ethyl acetate by them is concerned. In determining the order of efficiency of these catalysts for these reactions, the method of preparation of the catalyst is of an importance equal to, if not greater than the particular metal present in the oxide. Further, it is shown that the course of the decomposition of the ester is not determined by the relative instability of the intermediate compounds formed between the catalyst and the acid and the catalyst and the alcohol. The probability is that saponification of the ester precedes the decomposition. A sample of unignited alumina prepared from the hydroxide was found to exert a marked condensing action on acetone at 455° .

W. G.

The Successive Stages in the Hydrolysis of Triacetin. E. YAMAZAKI (*J. Amer. Chem. Soc.*, 1922, **44**, 426; cf. A., 1920, i, 591).—The author acknowledges the priority of Meyer's work (A., 1907, i, 819; 1909, ii, 391, 803) on this subject. W. G.

The Formation of Salts of Sulphocarboxylic Acids. I. Cobaltous and Cupric Salts of Sulphoacetic and α -Sulphopropionic Acids. H. J. BACKER and J. V. DUBSKÝ (*Rec. trav. chim.*, 1922, **41**, 145—151).—The cobaltous and cupric salts of sulphoacetic and α -sulphopropionic acids show almost complete similarity in behaviour, the only differences observed being in respect of the quantity and stability of water content. One molecule of the water of crystallisation of the neutral and acid copper salts is very strongly bound and the suggestion is made that this is linked to the sulphonic group. The neutral salts of both metals combine with two molecules of pyridine and the additive products also retain a molecule of water, probably linked in a similar manner to the above; the water is lost more easily by the additive products than by the neutral salts. The authors consider that the metal, rendered more positive by the presence of pyridine, may show greater affinity for the sulphonic group. The following have been prepared: *Cobalt sulphoacetate*, reddish-violet crystals; with two molecules of pyridine gives a light reddish-violet crystalline powder and, with a second molecule of the acid, light orange-red crystals of the acid salt; *cobalt α -sulphopropionate* was obtained only as a syrupy solution; with two molecules of pyridine, light violet crystals of the additive product crystallised; with a second molecule of the acid hygroscopic crystals of the acid salt of a light orange-red colour were obtained. *Copper sulphoacetate* forms small bluish-green crystals; with two molecules of pyridine it yields a deep blue, crystalline precipitate; with excess of acid, light bluish-green crystals of the acid salt. *Copper α -sulphopropionate* forms light blue crystals, which give with two molecules of pyridine deep blue crystals of the additive compound and, with a second molecule of the acid, light blue, hygroscopic crystals of the acid salt.

H. J. E.

Studies of the Constitution of Soap Solutions. Solutions of Sodium Palmitate, and the Effect of Excess of Palmitic Acid or Sodium Hydroxide. JAMES WILLIAM MCBAIN, MILLICENT TAYLOR, and MARY EVELYN LAING (*T.*, 1922, **121**, 621—633).

Colophenic Acids. W. FAHRION (*Ber.*, 1922, **55**, [B], 709; cf. Fahrion, A., 1907, i, 329; 1921, i, 792; Aschan, A., 1912, i, 512; this vol., i, 221).—The different varieties of colophony contain a large but unknown number of resin acids, all of which, in so far as they have been isolated, possess the formula $C_{20}H_{30}O_2$ and are soluble in light petroleum. They are all converted by atmospheric oxygen into darker coloured, amorphous autoxidation products which are insoluble in light petroleum and are classed as oxyacidic acids.

H. W.

The Catalytic Decomposition of Oleic Acid. ALPHONSE MAILHE (*Compt. rend.*, 1922, **174**, 873—874).—When oleic acid vapours are passed over a copper-aluminium alloy at 600—650°, they are decomposed, giving gases rich in hydrocarbons of the

series C_nH_{2n+2} and C_nH_{2n} and in hydrogen, and also a liquid rich in unsaturated hydrocarbons, which when hydrogenated by passage over nickel at $180-200^\circ$ give a mixture of aliphatic and aromatic hydrocarbons, among the latter of which benzene, toluene, and *m*-xylene were identified. W. G.

The Catalytic Decomposition of Shark Oil. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1922, [iv], 31, 249-252).—The method used for vegetable oils has been applied to shark oil as an example of animal oils (cf. A., 1921, i, 706, 841). The vapours of shark oil were passed over a mixture of aluminium and copper at $600-650^\circ$ and gaseous and liquid products were obtained. The former consisted of some acetaldehyde together with hydrocarbons and hydrogen. The latter contained acids, after the removal of which a yellow oil was left which, on hydrogenation over nickel at $180-200^\circ$, gave a mixture of paraffins, cyclic hydrocarbons of the type of cyclohexane and methylcyclohexane, and aromatic hydrocarbons, of which benzene, toluene, and *m*-xylene were identified. The acids referred to above were unsaturated, and after hydrogenation of the mixture over nickel at $230-240^\circ$ heptonic, pelargonic, and lauric acids were identified. W. G.

The Unsaturated Fatty Acids of Liver Lecithin. P. A. LEVENE and H. S. SIMMS (*J. Biol. Chem.*, 1922, 51, 285-294).—From the product of bromination of the fatty acids obtained from liver lecithin, an octobromoarachidic acid was isolated. When reconverted into a tetra-unsaturated acid, this yielded arachidonic acid, whilst the latter, on reduction, gave arachidic acid. The residue from the bromination, on similar treatment, gave first oleic and then stearic acid. On the assumption that arachidonic and oleic acids are the only unsaturated acids present in liver lecithin, it is calculated from the iodine numbers that lecithin obtained by extraction of liver with acetone contains oleic and arachidonic acids in the ratio 1.3:1, whilst the ratio for that extracted by ether is 4.3:1 (cf. A., 1921, i, 842). E. S.

Geometrical Isomerism in Unimolecular Films. N. K. ADAM (*Nature*, 1921, 107, 522; cf. A., 1921, ii, 488 and Langmuir, A., 1917, ii, 525).—In the case of certain fatty acids containing an ethylenic linking, the properties of films (considered to be one molecule in thickness) formed on the surface of water exhibit striking differences between *cis*- and *trans*-forms. It is thereby indicated that oleic and erucic acids are *cis*-forms, whilst elaidic and brassidic acids are *trans*-forms. It is considered that the molecules of saturated acids, such as palmitic acid, are attracted to the water by the carboxyl groups, whereas unsaturated acids are also attracted, although less powerfully, by their ethylenic linkings. The tendency of *cis*-forms to yield films of smaller area than those of the *trans*-forms is ascribed to the ability of the double bond in the former case to approach as closely as desired to the water, whilst in the latter case the saturated portion of the chain must be forced among the water molecules. Hence, owing

to the resistance produced by the limited flexibility of a hydrocarbon chain, the double bond of the *trans*-form will be unable to approach the water so closely as that of the *cis*-form. The area occupied by one molecule of a film of oleic acid on water under a compression of about 1.4 dynes per sq. cm. is of the order of 40×10^{-16} sq. cm., the area decreasing with time; elaidic acid occupies about 30×10^{-16} sq. cm., also diminishing with time.

A. A. E.

Preparation of Sodium Silver-thioglycolate. CHEMISCHE FABRIK FLORA (Brit. Pat. 156103).—Thioglycollic acid is treated with an equivalent quantity of a water-soluble silver salt and an excess of a solution of sodium hydroxide. Either reagent may be employed first, but if the former, the yellow precipitate of silver-thioglycollic acid, $\text{AgS}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which is formed, is separated and washed, and then dissolved in the soda solution. The sodium salt, $\text{AgS}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$, is exceedingly soluble in water, and is isolated by precipitation with alcohol as a heavy, yellow powder. It is of value for the therapeutic treatment of gonococci diseases.

G. F. M.

β -Halogen-substituted Fatty Acids and β -Lactones. HJALMAR JOHANSSON and SIDNEY M. HAGMAN (*Ber.*, 1922, **55**, [B], 647—658).—In continuation of the study of β -lactones (cf. Johansson, *Diss., Lund.*, 1916), α -methyl- β -butyrolactone and α -ethyl- β -butyrolactone are now described. The formation of β -lactones appears to occur much more commonly than was supposed formerly. From the preparative point of view, it is important to note that the hydrolysis of β -lactones to the hydroxy-acids is an irreversible process, whereas with γ -lactones the change is reversible; the successful production of the former from the β -halogenated acids depends, therefore, on their removal from solution before they have been converted to the hydroxy-acids. It has been observed previously (*loc. cit.*) that the hydrolysis of β -lactones (propiolactone, isobutyrolactone, and β -butyrolactone) is influenced but little if at all by the hydrogen-ion concentration. The behaviour of the present lactones is very analogous, but the action is not strictly unimolecular, and distinct evidence of hydrogen-ion catalysis is obtained. Apparently the process is complicated by simultaneous or consequent actions. In the presence of the resultant hydroxy-acid, the change appears to be uniformly unimolecular, but towards its end carbon dioxide and a gas resembling coal gas in odour are evolved; the full description of the experiments is reserved for a subsequent communication.

The preparation of β -bromo- α -methylbutyric acid, m. p. 63—64°, from tiglic acid and hydrogen bromide is described in detail. The hydrolysis of its sodium salt by water has been studied by arresting the reaction at definite intervals by pouring an aliquot portion of the solution on pure ice and titrating rapidly, first with sodium hydroxide and phenolphthalein and subsequently with silver nitrate and potassium chromate. The results show that no acid, with the exception of carbonic, is produced. Direct estimation of

q^*

the latter shows that two-thirds of the acid is transformed into carbon dioxide and Δ^3 -butene, whereas one-third is available for the production of the lactone. The latter is conveniently isolated by violently agitating a concentrated aqueous solution of sodium β -bromo- α -methylbutyrate with chloroform at about 30° , the organic medium being renewed from time to time and the neutrality of the solution being maintained by the addition of small crystals of sodium carbonate. It is a colourless, highly-refractive liquid, b. p. $67-67.5^\circ/21$ mm., d^{20} 0.9862; it solidifies at about -30° and melts at about -24° .

β -Bromo- α -ethylbutyric acid, m. p. 25° , is hydrolysed in neutral solution in much the same manner as the lower homologue, about 63% of it being converted into amylene and carbon dioxide, leaving about 37% available for the formation of the corresponding lactone. α -Ethyl- β -butyrolactone, $\text{CHEt} \begin{smallmatrix} \text{CHMe} \\ \text{CO} \end{smallmatrix} \text{O}$, is a colourless, mobile liquid, b. p. $79-81^\circ/18$ mm., d^{20} 0.9700. It does not solidify completely at -50° , but is not completely re-melted below -25° . 2.46 Grams of it are soluble in 100 c.c. of water at the atmospheric temperature. H. W.

Metallic Compounds of the Enolic Forms of Carbonyl Compounds and their Application to Syntheses. II. Synthesis of Vinylideneglycol Diethyl Ether [Keten-acetal]; Explanation of the Course of the Reaction in the Acetoacetic Ester Synthesis. HELMUT SCHEIBLER and HEINRICH ZIEGLER (*Ber.*, 1922, 55, [B], 789-803; cf. Scheibler and Voss, A., 1920, i, 366).—The product obtained by the condensation of ethyl acetate with metallic sodium or sodamide does not appear to be composed mainly of ethyl sodioacetoacetate or of the compound $\text{OEt} \cdot \text{CMe}(\text{ONa}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, but of the substance $\text{COMe} \cdot \text{CH}_2 \cdot \text{C}(\text{OEt})_2 \cdot \text{ONa}$.

When decomposed by dilute acids, it yields ethyl acetoacetate and alcohol, $\text{COMe} \cdot \text{CH}_2 \cdot \text{C}(\text{OEt})_2 \cdot \text{ONa} \rightarrow \text{COMe} \cdot \text{CH}_2 \cdot \text{C}(\text{OEt})_2 \cdot \text{OH} \rightarrow \text{COMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} + \text{EtOH}$; by spontaneous decomposition of its ethereal suspension or by the action of water, it is converted into sodium acetate and ketenacetal: $\text{COMe} \cdot \text{CH}_2 \cdot \text{C}(\text{OEt})_2 \cdot \text{ONa} \rightarrow \text{CH}_3 \cdot \text{C}(\text{OEt})_2 + \text{CH}_3 \cdot \text{CO}_2\text{Na}$.

The gradual addition of ethyl benzoate to a suspension of ethyl potassioacetate in anhydrous ether causes the slow separation of considerable quantities of potassium benzoate. The ethereal filtrate is treated with water and the aqueous portion yields ethyl benzoyleacetate, whereas the ethereal portion contains unchanged ethyl benzoate, unsaturated ethers, a hydrocarbon of high boiling point which will be described subsequently, and the ketenacetal which could not be isolated as such from this mixture. The change may be represented by the scheme: $\text{CH}_3 \cdot \text{C}(\text{OK}) \cdot \text{OEt} + \text{Ph} \cdot \text{CO}_2\text{Et} \rightarrow \text{CH}_2\text{Bz} \cdot \text{C}(\text{OEt})_2 \cdot \text{OK} \rightarrow \text{CH}_3 \cdot \text{C}(\text{OEt})_2 + \text{Ph} \cdot \text{CO}_2\text{K}$. The course of the reaction is here somewhat disturbed by the occurrence of hydrogenation, but this drawback is not experienced when the potassium is replaced by sodamide. A reaction does not occur

when ethyl benzoate is added to finely divided sodamide covered with ether, but the gradual introduction of ethyl acetate causes vigorous evolution of ammonia; the precipitate contains sodium benzoate, sodium acetate, and benzamide, but the isolation of ketenacetal from the filtrate is difficult. The accomplishment of the latter depends on the observation that the decomposition of the sodium salt can be effected more conveniently by means of water than by spontaneous fission in ethereal suspension; the use of ethyl benzoate and ether is thereby rendered unnecessary, and it is more practical to operate with ethyl acetate alone, the excess of which plays the part of solvent. Powdered sodamide is therefore added in small portions to freshly distilled ethyl acetate cooled in a powerful freezing mixture; after some hours, the temperature is allowed to rise to 20°. The product is diluted with ether and gently warmed on the water-bath, after which the solvent and unchanged ethyl acetate are removed in a vacuum. The residual salt is gradually added to a small quantity of water at 20°, whereupon sodium acetate separates gradually. The *ketenacetal* is extracted from the filtrate with ether. It is a volatile liquid with a faint ethereal odour, b. p. 77.5–78°, 760 mm., d^{22}_4 0.7938, $[R_L]^{21}_D$ 32.54, $[R_L]^{21}_D$ 32.65, $[R_L]^{21}_D$ 33.05. It is readily oxidised by alkaline permanganate and rapidly decolorises bromine dissolved in carbon tetrachloride. It is comparatively stable towards alkali hydroxide, but is decomposed by mineral acids into ethyl acetate and ethyl alcohol. It reacts very readily in ethereal solution with the alkali metals or their amides. Its relationship to the keten-acetals appears to be purely formal, since it differs widely in its properties from substances such as acroleinacetal and behaves rather as unsaturated ether.

H. W.

Trihalogenmethyl Reactions. IV. Reaction of Trichloroacetic Acid with Copper. HOWARD WATERS DOUGHTY and BENJAMIN FREEMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 636–645; cf. A., 1918, i, 57; 1919, i, 513; 1921, ii, 414).—When ethyl trichloroacetate is warmed on a water-bath with copper powder, it gives *diethyl tetrachlorosuccinate*, b. p. 156°, 13 mm. Attempts to hydrolyse the ester were not successful. Trichloroacetic acid reacts very vigorously with copper powder, but tetrachlorosuccinic acid could not be isolated in the pure state, only its *aniline* salt, m. p. 149–150° (corr.) being prepared. In benzene or water as solvent, trichloroacetic acid reacts with copper, giving a good yield of dichloroacetic acid and this method is recommended as a means of preparing dichloroacetic acid in any desired quantity.

There is some indication that these reactions involve the formation of a relatively unstable intermediate compound in which copper is directly linked to carbon, and that the course of the reaction is determined by the manner in which the copper is eliminated from this intermediate compound.

W. G.

The α -Alkyl-levulic Acids. H. GAULT and T. SALOMON (*Compt. rend.*, 1922, **174**, 754–756).— α -Alkyl-levulic acids may readily be prepared by the following series of reactions. The sodium

q* 2

derivative of diethyl malonate reacts with bromoacetone in ether to give diethyl acetonylmalonate, $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$, b. p. $150^\circ/20$ mm., giving a phenylhydrazone, m. p. $108-109^\circ$, and a semicarbazone, m. p. $125-127^\circ$. At the same time, a certain amount of ethyl ethanetetra-carboxylate is also formed. The sodium derivative of the acetonylmalonic ester readily condenses with alkyl iodides to give alkylacetonylmalonic esters, of which the following are described: Ethyl ethylacetonylmalonate, giving a phenylhydrazone, m. p. $99-100^\circ$; and ethyl isobutylacetonylmalonate, giving a phenylhydrazone, m. p. $72-73^\circ$. These esters saponify more or less readily, giving the free acids. Ethylacetonylmalonic acid, m. p. $122-123^\circ$, gives a phenylhydrazone, m. p. $136-137^\circ$, but the isobutyl acid was not obtained pure owing to the difficulty of removing the second ester group. The free acids, when heated, readily lose a molecule of carbon dioxide, giving the corresponding α -alkyl-levulic acid, and the ester acids also lose carbon dioxide, giving ethyl α -alkyl-levulates.

W. G.

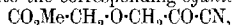
Diglycollic Acid or Anhydroglycollic Acid. RICHARD ANSCHÜTZ and SIEGFRIED JAEGER (*Ber.*, 1922, 55, [B], 670-679).—In connexion with the recent publication by Sido (A., 1921, i, 447) on cyclic imide ethers of diglycollic acid as sweetening agents, the authors describe a series of similar products.

The following diglycollarylamic acids are prepared by treating a solution of diglycollic anhydride in chloroform with an equivalent quantity of the requisite amine dissolved in the same solvent. Diglycollanilic acid, m. p. 118° ; diglycoll-*o*-, -*m*-, and -*p*-toluidic acids, slender needles, m. p. 120° , needles, m. p. $131-132^\circ$, and leaflets or long needles, m. p. 148° , respectively; diglycoll-*p*-xylic acid, flat plates, m. p. 106° ; diglycoll-*as-m*-xylic acid, slender needles, m. p. $116-117^\circ$; diglycoll-1:2:4:5- ψ -cumidic acid, slender needles, m. p. $133-135^\circ$; diglycoll- α -naphthalidic acid, needles, m. p. 165° ; diglycoll- β -naphthalidic acid, microscopic needles, m. p. 153° . Treatment of the arylamidic acids with boiling acetyl chloride results in the formation of the corresponding arylimides, of which the following are described: diglycollanil, m. p. 195° ; *o*-tolil, m. p. 126° ; *m*-tolil, m. p. 114° ; *p*-tolil, m. p. 186° ; diglycoll-*p*-xylic acid, flat, hexagonal plates, m. p. 127° ; diglycoll-*as-m*-xylic acid, needles, m. p. 102° ; diglycoll- α -naphthil, m. p. 176° ; diglycoll- β -naphthil, four-sided rods, m. p. 172.5° .

Diglycollic anhydride is converted by hydrazine into the hydrazidic acid, $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, slender needles, m. p. $113-114^\circ$; the corresponding hydrazine and silver salts have been prepared.

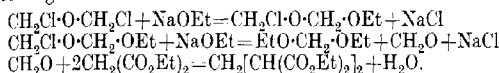
Methyl diglycollate, b. p. $130^\circ/13$ mm., m. p. 36° , is prepared by dissolving diglycollic anhydride in an excess of methyl alcohol and subsequently saturating the mixture with hydrogen chloride. Methyl hydrogen diglycollate, a colourless, viscous liquid which solidifies in a freezing mixture, b. p. $173-174^\circ/12$ mm., is prepared from the anhydride and methyl alcohol and is converted by thionyl chloride into the corresponding chloride, a mobile liquid,

b. p. 107–108°/12 mm., 114–115°/15 mm., from which the following derivatives are prepared: *anilide*, a pale yellow oil, b. p. 175–180°; *o-toluidide*, a yellow liquid, b. p. 185°/13 mm.; *p-toluidide*, slender, colourless needles, m. p. 41°. The chloride is transformed by silver cyanide into the corresponding *cyanide*,



a colourless, heavy liquid, b. p. 165–170°/16 mm., which is hydrolysed by fuming hydrochloric acid at the atmospheric temperature to the *acid*, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$, m. p. 129–130°, b. p. 160°/13 mm.; the *silver* salt of the latter is described. H. W.

The Reaction between *s*-Dichlorodimethyl Ether and Ethyl Malonate. ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1922, **44**, 649–650).—Dichlorodimethyl ether reacts with the sodium salt of ethyl malonate to give ethyl propanoxy-tetracarboxylate together with some methylene dimethyl ether (cf. Kamm and Waldo, this vol., i, 105). It is probable that in this reaction the sodium functions as sodium ethoxide and not as the sodium salt of ethyl malonate, the reaction occurring in three stages.



W. G.

Sulphur in Proteins. I. The Effect of Acid Hydrolysis on Cystine. WALTER FRED HOFFMAN and ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1922, **44**, 341–360).—Pure cystine, crystallising in hexagonal plates, was boiled for varying lengths of time up to one hundred and ninety-two hours with 20% hydrochloric acid. The analytical data indicate that cystine is only slowly decomposed or destroyed during prolonged boiling with 20% hydrochloric acid and there would not be any appreciable decomposition during an ordinary protein hydrolysis. During the one hundred and ninety-two hours' boiling there was but little decarboxylation. Similarly, the sulphur of the cystine was not eliminated to any appreciable extent. A small amount of hydrogen sulphide was evolved, some elementary sulphur separated, but no sulphates were formed, and about 90% of the original sulphur was still unchanged and unoxidised at the end of the period of boiling. The amount of cystine precipitable by phosphotungstic acid decreased rapidly during the first forty-eight hours of boiling, after which it remained practically constant. The nitrogen of the cystine was not appreciably changed during the boiling. The amount of total nitrogen remained constant, the amount of amino-nitrogen slowly decreased and there was a corresponding slowly progressive increase in the amount of ammonia nitrogen. The optical rotation of the cystine solution rapidly fell during the boiling to complete inactivity at the end of ninety-six hours. From the residual hydrolysate an isomeric cystine was isolated. It crystallised in small, microscopic prisms and differed in its

physical and chemical properties from the original cystine. It was approximately 2.5 times as soluble in water, and its phosphotungstate was four times as soluble. It was optically inactive. A number of derivatives of the two forms of cystine were prepared, and in every instance the isomeric derivatives possessed different properties from those prepared from the natural "plate" cystine. The authors suggest that this isomeric cystine which they have isolated is identical with that synthesised by Fischer and Raske (A., 1908, i, 325) and by Erlenmeyer and Stoop (A., 1905, i, 119), and that the "plate" cystine obtained by protein hydrolysis has never been synthesised.

W. G.

Resolution of Hydroxyaspartic Acids [Aminohydroxysuccinic Acids] into Optically Active Forms. H. D. DAKIN (*J. Biol. Chem.*, 1922, 50, 403-411).—Resolution of the anti-acid (cf. this vol., i, 143) was effected by fractional crystallisation of its strychnine and quinine salts, which yielded *strychnine* d-anti-aminohydroxysuccinate ($4\text{H}_2\text{O}$, $[\alpha]_D^{20} -19.1^\circ$) and *quinine* l-anti-aminohydroxysuccinate ($4\text{H}_2\text{O}$, $[\alpha]_D^{20} -95.5^\circ$), respectively. By regeneration of the acids from these salts, d-anti-aminohydroxysuccinic acid, wedge-shaped prisms, $[\alpha]_D^{20} +12.1^\circ$, and l-anti-aminohydroxysuccinic acid, wedge-shaped prisms, $[\alpha]_D^{20} -11.9^\circ$, were obtained. Both active forms gave mesotartaric acid on treatment with nitrous acid, whilst heating with water at 125° produced a partial conversion into the inactive para-acid. Attempts to resolve the para-acid were unsuccessful. Fractional crystallisation of the following alkaloid salts: *strychnine* ($3\text{H}_2\text{O}$, prisms, $[\alpha]_D^{20} -23.2^\circ$), *cinchonine* (aq., hexagonal prisms, $[\alpha]_D^{20} +122.5^\circ$), *brucine* ($4\text{H}_2\text{O}$, thin plates, $[\alpha]_D^{20} -23.4^\circ$), *quinine* ($2\text{H}_2\text{O}$, felted needles, $[\alpha]_D^{20} -116^\circ$), and the action of *Penicillium glaucum* on the sodium salt, were tried but without result. A partial resolution appeared to be effected by fermenting yeast, the lævo-acid being preferentially consumed. The amount of resolution, however, was too small to render possible the isolation of the active acid.

From an investigation of the products obtained by the tryptic digestion of casein it is concluded that aminohydroxysuccinic acid does not occur in this protein (cf. Skraup, A., 1904, i, 539).

E. S.

Preparation of Acetaldehyde and Acetic Acid. A. WOHL (Brit. Pat. 154,579).—In the catalytic hydration of acetylene to acetaldehyde, mercury salts may be replaced by salts of heavy metals which are not appreciably volatile and are not transformed into oxides at temperatures below a red heat. The best results are obtained with basic zinc salts deposited on pumice and maintained at about 360° , the basic vanadate being preferably employed, but the molybdate or chromate may be used, as also may the corresponding salts of copper, cobalt, nickel, or cadmium, but not with such good results. The acetylene is mixed with a considerable excess of air and steam, and under favourable conditions 75-80% of the theoretical yield of acetaldehyde together with 5% of acetic acid are obtained.

G. F. M.

Synthesis and Properties of a δ -Hydroxyaldehyde. BURCKHARDT HELFERICH and THEODOR MALKOMES (*Ber.*, 1922, **55**, [B], 702—708).— δ -Hydroxyhexaldehyde has been synthesised in a manner similar to that used previously for γ -hydroxyvaleraldehyde (Helferich, A., 1920, i, 11). Like the γ -hydroxyaldehydes described previously, the new aldehyde appears to be stable in the cyclic form, $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 - \text{CHMe} \\ \text{CH}_2 \cdot \text{CH(OH)} \end{smallmatrix} > \text{O}$, but to pass readily in the course of various reactions into the true aldehyde form, $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHO}$. The observations appear to be of considerable importance for the chemistry of the sugars, since the possibility of the formation of 1:5-rings (in place of the generally assumed 1:4-structures) must be taken into account.

Δ^5 -Hexenoic acid is prepared from cyclohexanone oxime by Wallach's method (a lactone, $\text{C}_6\text{H}_{10}\text{O}_2$, b. p. 96.5°–97.5°/15 mm., is obtained as by-product) and is converted by thionyl chloride into Δ^5 -hexenoyl chloride, a colourless, mobile liquid, b. p. 49°/17 mm., d_4^{25} 1.0113, n_D^{25} 1.4471. The latter is transformed by magnesium methyl iodide into methyl Δ^5 -amylenyl ketone, $\text{CH}_3 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COMe}$, a colourless liquid of unpleasant odour, b. p. 41–43°/10 mm., d_4^{25} 0.8673, n_D^{25} 1.4350 (semicarbazone, aggregates of needles, m. p. 108°), which is reduced to methyl- Δ^5 -amylenyl-carbinol, a colourless liquid, b. p. 64–65°/13 mm., d_4^{25} 0.8484, n_D^{25} 1.4387. Ozonisation of the latter and subsequent reduction of the ozonide in ethereal solution with zinc dust and glacial acetic acid give δ -hydroxy-*n*-hexaldehyde (or 6-hydroxy-2-methyltetrahydropyran, b. p. 71–78°/11 mm., d_4^{25} 1.0063, n_D^{25} 1.4452). The cyclic structure of the aldehyde is established by its physical constants and the observation that it reduces ammoniacal silver solution and colours magenta-sulphurous acid solution gradually. It gives a *p*-bromophenylhydrazone, small, pale yellow needles, m. p. 85° (slight decomp.), and is oxidised by silver oxide in the presence of water to δ -hydroxy-*n*-hexoic acid. It is converted by methyl alcoholic hydrogen chloride (1%) into 6-methoxy-2-methyltetrahydropyran, a colourless, mobile liquid with an odour of peppermint, b. p. 71.5°–76°/110 mm., d_4^{25} 0.9232, n_D^{25} 1.4211. The latter does not reduce Fehling's or ammoniacal silver solutions, and does not appear to be hydrolysed by emulsin or α -glucosidase from yeast.

H. W.

Preparation of Aldehydes from Acid Chlorides. V. (Di-aldehydes. II.) Synthesis of Decanedial. KARL W. ROSENMUND, FRITZ ZETTSCHIE, and FL. ENDERLIN (*Ber.*, 1922, **55**, [B], 609–612; cf. A., 1921, ii, 320; this vol., i, 39). *Decanedial* (sebacic dialdehyde), $\text{C}_8\text{H}_{16}(\text{CHO})_2$, is prepared in at least 80% yield by the action of hydrogen on a solution of sebacyl chloride in xylene at 150° in the presence of palladised kieselguhr and "sulphured" quinoline; it is a colourless, oily liquid with a pleasant odour, b. p. 142°/15 mm., which polymerises rapidly to a vitreous form. Both varieties give the usual aldehydic reactions with Fehling's solution, magenta-sulphurous acid and ammoniacal

silver solution. The sodium hydrogen sulphite compound and the barium salt, $C_8H_{16}(CH_3N \cdot C_{10}H_6SO_3)_2Ba$, formed from the aldehyde and barium naphthionate, are described. The aldehyde yields a *di-p-nitrophenylhydrazone*, tile-red crystals, m. p. 104—107° (decomp. after softening at about 95°), and a *dioxime*, slender, colourless needles, m. p. 124—127° (corr.) after previous softening; the latter does not appear to be identical with the similar compound described by von Braun and Sobecki (A., 1911, i, 830). H. W.

Spontaneous Condensation of Ethoxyacetone ; Formation of the Corresponding Aldol, α -Diethoxy- β -methylpentan- β -ol- δ -one. VICTOR DAUDEL (*Bull. Soc. chim.*, 1922, [iv], 31, 265—268).—Ethoxyacetone, as prepared by the action of magnesium methyl bromide on ethoxyacetonitrile, slowly undergoes condensation on keeping, probably due to traces of ammonia present. The principal product is α -diethoxy- β -methylpentan- β -ol- δ -one, $OEt \cdot CH_2 \cdot CO \cdot CH_2 \cdot CMe(OH) \cdot CH_2 \cdot OEt$, b. p. 126—128°/21 mm.; d^{20} 1.011. The condensation is, however, more complex and resinous products are formed which could not be identified. A compound, b. p. 170—180°/16 mm.; d^{20} 1.0164, was isolated.

W. G.

Influence of Sodium Chloride on the Mutarotation of Dextrose in Alkaline Solution. I and II. HANS MURSCHHAUSER (*Biochem. Z.*, 1922, 128, 215—228, 229—244).—I. In $N/2000$ -sodium carbonate solution the velocity of mutarotation of dextrose solutions is retarded by the presence of sodium chloride. The retardation is proportional to the square root of the concentration of the sodium chloride.

II. The velocity constants of the mutarotation of dextrose at 20.4° have been determined in aqueous solution, in 2*N*- and 4*N*-sodium chloride solution, in increasing concentrations of hydrochloric acid from 0.046 to 0.54% and in 2*N*- and 4*N*-sodium chloride solutions containing increasing amounts of hydrochloric acid from 0.046 to 0.54%. All follow the unimolecular law, and although at concentrations of acid below 0.089%, 2*N*- and 4*N*-sodium chloride lower the velocity of mutarotation compared with hydrochloric acid solutions below 0.089%, yet in all cases the velocity constants of the mutarotation, whether in hydrochloric acid solution alone or in 2*N*- or 4*N*-sodium chloride, increase proportionally to the concentration of hydrochloric acid.

H. K.

The Law Governing the Constants of Mutarotation of Dextrose and the Concentration of Acid. HANS MURSCHHAUSER (*Biochem. Z.*, 1922, 128, 243—250).—It has been shown (preceding abstract) that at constant temperature the increase in the velocity constant of the mutarotation of dextrose in the presence of increasing amounts of hydrochloric acid is proportional to the concentration of the acid, $K_{HCl} - K_{H_2O} = 48.5 C_{HCl}$ at 20.4°. If, however, the velocity constant in the presence of hydrochloric acid, K_{HCl} , be divided by the square root of the concentration of the hydrochloric acid (or the hydrogen-ion concentration), another

constant is obtained. The first equation given enables either the strength of a hydrochloric acid solution from the velocity constant or the reverse to be determined.

H. K.

The Formation of Formic Acid during the Decomposition of Dextrose in Alkaline Solution. H. I. WATERMAN and M. J. VAN TUSSEN BROEK (*Chem. Weekblad*, 1922, **19**, 135—136).—Solutions of dextrose in *N*-sodium hydroxide solution containing barium hydroxide were treated with ordinary air and with air containing ozone. In all cases formic acid was formed; 10 grams of dextrose after one hundred and forty-two and a half hours yielded 1.66 grams of the acid. No carbon dioxide was formed except when the temperature was kept below normal. S. I. L.

The Function of Phosphates in the Oxidation of Dextrose by Hydrogen Peroxide. ARTHUR HARDEN and FRANCIS ROBERT HENLEY (*Biochem. J.*, 1922, **16**, 143—147).—The chief function of phosphates in the oxidation of dextrose by hydrogen peroxide appears to be the regulation of the hydrogen-ion concentration as other buffer mixtures ($\text{NaHCO}_3 + \text{CO}_2$; $\text{Na}_2\text{HAsO}_4 + \text{NaH}_2\text{AsO}_4$; $\text{NaC}_2\text{H}_3\text{O}_2$; $\text{K}_2\text{HPO}_4 + \text{KH}_2\text{PO}_4$) can replace the phosphates. Hydrogen peroxide is more stable in presence of phosphates than at the same P_{H} in their absence. W. O. K.

Preparation of Mannose. E. P. CLARK (*J. Biol. Chem.*, 1922, **51**, 1—2).—The method described is simpler and gives better yields than those of Hudson and Sawyer (A., 1917, i, 321) and of Horton (*J. Ind. Eng. Chem.*, 1921, **13**, 1040). Sifted ivory-nut shavings are added to ten times their weight of boiling 1% sodium hydroxide and left for half an hour with occasional stirring. They are then thoroughly washed with water and dried. The material (500 grams) so obtained is mixed with an equal weight of 75% sulphuric acid and left for a day, after which the resulting mass is dissolved in water, diluted to $5\frac{1}{2}$ litres, and boiled for two and a half hours. The solution is then neutralised with barium carbonate paste and filtered through a thin layer of active carbon, the last traces of barium being removed by adding a few c.c. of dilute sulphuric acid and again filtering. The filtrate is concentrated until it contains 87—88% of total solids, mixed with an equal volume of glacial acetic acid, seeded, and frozen. Finally, it is allowed to thaw slowly in a refrigerator, when crystallisation of the mannose takes place.

E. S.

Crystalline Chlorotetra-acetylmannose. D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1922, **44**, 401—406; cf. Fischer and Hirschberger, A., 1889, 480, 687).—Chlorotetra-acetylmannose was obtained in a crystalline form by applying the method of von Arlt (cf. A., 1901, i, 369). Phosphorus pentachloride was allowed to act on β -penta-acetylmannose in the presence of aluminium chloride in chloroform. The product was obtained in crystals, m. p. 81° ; $[\alpha]_{\text{D}}^{20} + 89.50^\circ$. With methyl alcohol and silver carbonate, chlorotetra-acetylmannose gives a mixture of methyltetra-acetylmannoses, thus

resembling in this respect bromotriacetylrrhamnose, but differing from the corresponding derivatives of dextrose and galactose.

W. G.

The Constitution of Polysaccharides. J. J. LUNST ZWIKKER (*Rec. trav. chim.*, 1922, **41**, 152).—A correction is made in the formulæ given in the author's paper (this vol., i, 230); it is maintained that it necessitates no change in the suggested molecular structure.

H. J. E.

New Observations on the Constitution of the Carbohydrates. L. DE HOOP (*Chem. Weekblad*, 1922, **19**, 106—107).—The conclusions of Karrer, based on methylation and acetylation, that the starch molecule is really simpler than the earlier molecular-weight determinations (5,000 to 20,000) indicate, are criticised as being based on insufficient evidence.

S. I. L.

Preparation of Inulin, with Special Reference to Artichoke Tubers as a Source. J. J. WILLAMAN (*J. Biol. Chem.*, 1922, **51**, 275—283).—The ground and washed tubers are boiled for fifteen to twenty minutes with water containing calcium carbonate (1,300 c.c. of water and 30 grams of calcium carbonate to each kilo.) and the juice is then expressed in a press. After repeating the process on the residue, the combined extracts are clarified by means of lead acetate, any excess of the latter being removed by addition of ammonium oxalate. The clear liquid is then evaporated until it contains 40—60% of solids, cooled slowly, and maintained at 0—5° for crystallisation. Recrystallisation from water is repeated until the specific rotation reaches —38° or —39°. A study of the optical rotation during successive recrystallisations confirms the view that inulin is a mixture of substances. Artichoke tubers are not a good source of true inulin.

E. S.

Alleged Adsorption of Alumina from Aluminium Sulphate Solutions by Cellulose. ALFRED TINGLE (*J. Ind. Eng. Chem.*, 1922, **14**, 198—199).—Neither acid-washed filter-paper nor well-washed bleached sulphite pulp removes any analytically appreciable amounts of alumina from a basic solution of aluminium sulphate, and the observed withdrawal of alumina from solutions of the sulphate in presence of cellulose is due to chemical precipitation by non-cellulose material present as an impurity. In no case could adsorption of alumina by cellulose of reasonable purity be observed. Methods of investigation which depend on attempts to separate aluminium salts from cellulose by repeated washing can only be employed when great caution is used as to the nature of the materials, and when basic solutions are in question they can never be trusted, as mere dilution of a basic aluminium sulphate solution will cause precipitation.

G. F. M.

Action of Iodine on Celluloses, Silk, and Wool. J. HUEBNER and J. N. SINHA (*J. Soc. Chem. Ind.*, 1922, **41**, 93—94r).—Celluloses, natural and artificial silk, wool, and other like substances give varying but appreciable yields of iodoform when treated with dilute aqueous solutions of iodine and potassium iodide. The

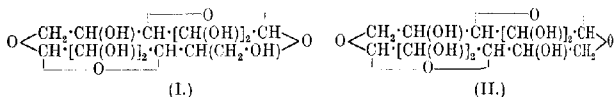
reaction was most marked with poplar wood cellulose, and by distilling with steam poplar cellulose pulp to which iodine and sodium hydroxide had been added pure iodoform was readily obtained. The operation could be repeated and even after twenty successive treatments appreciable yields of iodoform were obtained. The results seem to indicate that the amount of iodoform produced has some definite relation to the solubility of the different celluloses in alkali hydroxide solutions. G. F. M.

Effect of Water and certain Organic Salts on Celluloses. J. HUEBNER and F. KAYE (*J. Soc. Chem. Ind.*, 1922, **41**, 94r).—Distilled water in which purified cotton or cellulose has been soaked at 35° for twenty-four hours readily gives a silver mirror and the characteristic aldehyde reaction with rosaniline, whilst if it is steeped in sodium acetate solution under similar conditions the amount of aldehyde produced is so considerable that it can be separated by distillation. If the cotton is merely placed over distilled water in a closed vessel for several days, the water, without having come into contact with the cellulose, contains traces of aldehydic substances. If cellulose or starch remains for several days in contact with distilled water at 35° to which sodium acetate and resorcinol have been added, the solution becomes fluorescent and aldehydic substances can be separated by distillation, whilst the addition of lead acetate to the residue after distillation causes a greyish-brown precipitate. When cellulose is steeped in water there is a rise of temperature accompanied by a contraction of the total volume. G. F. M.

Polysaccharides. XIV. The Amyloses. P. KARRER and ELISABETH BÜRKLIN (*Helv. Chim. Acta*, 1922, **5**, 181—187; cf. this vol., i, 229).—The behaviour of Pringsheim's "triamylose" towards acetyl bromide at 0—5° is similar to that of α -diamylose and β -hexamylose, since it furnishes the same quantities of aceto-bromomaltose and heptacetylmaltose as the corresponding amount of maltose. No glucose could be detected among the products. "Triamylose" is therefore either a simple or a polymeric form of maltose anhydride. Its identity with β -hexamylose is established by a comparison of their solubilities, specific rotatory powers, crystalline form, contents of water of crystallisation, indifference to pancreatic juice, and compounds with sodium hydroxide. So far, therefore, all methods of degrading starch have furnished either maltose or simple or polymeric forms of its anhydride. Also the fact that the acetylation of β -hexamylose with acetic anhydride and zinc chloride proceeds without depolymerisation opens up the possibility of avoiding such degradation in the cases of starch, cellulose, etc., in which more or less complete breaking down has hitherto been accepted. J. K.

Polysaccharides. XV. Constitution of Diamylose and of the Anhydro-sugar (Cellosan) of Cellulose. P. KARRER and ALEX. P. SMIRNOV (*Helv. Chim. Acta*, 1921, **5**, 187—201; cf. preceding abstract).—Treatment of penta-acetyl-glucose with

phosphorus pentabromide (5 parts) for twelve minutes at 100° yields considerable amounts of tetraceto-1-bromoglucose, but no 1 : 6-dibromo-derivative. In agreement with this, the same product is obtained from octa-acetylcellulobiose, whilst from octa-acetyl-maltose aceto-1 : 6-dibromo- and aceto-1-bromo-glucose are obtained. From acetylated diamylose, on the other hand, aceto-1 : 6-dibromoglucose, unaccompanied by any monobromo-derivative, is produced. Hence, in diamylose, the anhydro-oxygen atom connects the 1- with one of the 8-, 9-, 11-, or 12-carbon atoms of the maltose molecule. Since starch is a polymeric diamylose, its acetyl derivative also furnishes aceto-1 : 6-dibromoglucose as sole product. "Triacetyl-cellulose" (Ost, *Z. angew. Chem.*, 1919, 67) behaves similarly, a result irreconcilable with the view that the cellulose molecule consists of a chain or cyclic structure of cellobiose molecules, but in accordance with its conception as a polymeric anhydrocellobiose (*Cellulosechemie*, 1921, 2, 125). This anhydride, now termed cellosan, must therefore have the constitution (I). This formula at once explains the formation of 2 : 3 : 6-trimethyl-glucose, instead of tetramethylglucose, from methylated cellulose. Further, it also represents cellosan as an anhydride of maltose (or isomaltose), so that its degradation may occur in two ways— to cellobiose or to maltose. Hence it is that only 40–43% (or, allowing for that portion which suffers further degradation, at most 50–60%) of acetocellobiose is obtainable by acetolysis of cellulose (Karrer and Widmer, A., 1921, i, 310; Freudenberg, A., 1921, i, 400). The easy hydrolysis of maltose by acids explains the failure to detect its formation either in this reaction or among the products of the action of acetyl bromide on cellulose (A., 1921, i, 771). Of the three remaining possible formulae for diamylose, that of the 1–12 anhydride (II) is alone acceptable. It explains



the complete conversion of starch and diamylose into maltose, since the same result must follow from the rupture of either of the two glucosidic linkings. Steric influences may possibly influence the stabilities of diamylose and cellulose, but the easier hydrolysis of the former is adequately explained by the fact that in it the alcoholic groups concerned in the glucosidic linkings are both primary. It now only remains to determine what degrees of polymerisation of cellosan and diamylose are respectively represented by cellulose and starch.

The aceto-mono- and -dibromo-glucoses obtained in the above reaction are always accompanied by oily products, consisting probably of the isomeric acetodibromoglucoses, the formation of which is to be anticipated, other bromination (cf. Brigl, this vol., i, 225) and decomposition products, and also undecomposed diacetyl- and acetyl- complexes.

J. K.

Structure and Formation of the Humic Acids and Coal.

J. MARCUSSEN (*Z. angew. Chem.*, 1922, **35**, 165—166; cf. this vol., i, 326).—Polemical. The author maintains that humic acids contain condensed furan and benzene rings and stand in close relationship to, if they are not identical with, the synthetic acids prepared from sugars. Contrary to Eller's views (*loc. cit.*), these acids are carboxylic acids, as are also most probably the acids synthesised by Eller from phenols, and both probably contain a dibenzofuran nucleus. Eller's acids are, however, in no way identical with the natural humic acids, as evidenced by their hydrogen content and their behaviour towards soda. In the conversion of humic acids into brown coal, anhydride formation accompanied by loss of carbon dioxide occurs, and this so-called pyrohumic acid was isolated from brown coal after the extraction of the humic acids with ammonia by boiling the insoluble residue with 10% sodium hydroxide, and the lesser number of carboxyl groups found expression in the lower saponification value, 253, compared with 300 for humic acid. In coal formation, the author considers that cellulose as well as lignin plays a part, and although a portion is undoubtedly destroyed by bacterial action, this cannot apply to the whole of the cellulose associated with the lignin in wood.

G. F. M.

Amides and Anilides of some Saturated Fatty Acids.

MITZÛ ASANO (*J. Pharm. Soc. Japan*, 1922, 97—105).—As the amides and anilides of fatty acids are of use in the detection and identification of these acids, whilst the melting points given in the literature are discordant, the author has prepared some of them together with the isobutylamides from the pure acids (from heptioic acid to lauric acid) and determined their melting points, the result being as follows: Heptioic acid: amide, m. p. 94—95°; anilide, m. p. 64°. Octoic acid: amide, m. p. 104°; anilide, m. p. 51.5°; isobutylamide, b. p. 154—155°/7 mm. Pelargonic acid: amide, m. p. 99°; anilide, m. p. 57.5°; isobutylamide, b. p. 162°/6 mm., m. p. 37—38°. Decoic acid: amide, m. p. 98°; anilide, 67—68°; isobutylamide, b. p. 171°/6 mm.; m. p. 37—38°. Undecoic acid: amide, m. p. 96—97°; anilide, m. p. 68°; isobutylamide, m. p. 51°. Lauric acid: amide, m. p. 98—99°; anilide, 75°; isobutylamide, m. p. 51°.

K. K.

Syntheses from Cyanamide. Preparation of Thiocarbamine Cyanides, Carbamine Cyanides, and Biurets.

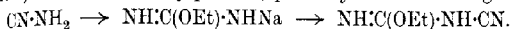
FROMM [with HERMANN WENZL] (*Ber.*, 1922, **55**, [B], 804—813).—The product of the action of sodium cyanamide on phenylthiocarbimide has the constitution $\text{NPh}\cdot\text{C}(\text{SNa})\cdot\text{NH}\cdot\text{C}\cdot\text{N}$, since it is converted by benzyl chloride into the compound $\text{NPh}\cdot\text{C}(\text{S}\cdot\text{C}_6\text{H}_5)_2\cdot\text{NH}\cdot\text{CN}$, which has been obtained from phenyldithiobiuret, benzyl chloride, and sodium hydroxide. The benzyl haloid has, in addition, a desulphurising action which is due to the disturbance of the equilibrium, $\text{X}\cdot\text{C}(\text{NH})\cdot\text{SNa} \rightleftharpoons \text{X}\cdot\text{C}\cdot\text{N} + \text{NaSH}$, by the removal of the sulphide. This desulphurising effect is considerably more marked with ethylene chlorohydrin, which, with phenyldithio-

biuret or the product of the action of sodium cyanamide and phenylthiocarbimide, gives phenylcarbamine cyanide, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CN}$, *s*-diphenylcarbamide, and triphenylisomelamine, $(\text{NHPh}\cdot\text{CN})_3$. The initial change is doubtless expressible by the equations $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2 + 2\text{NaOH} \rightleftharpoons \text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{CN} + \text{Na}_2\text{S} + 2\text{H}_2\text{O}$ and $2\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl} + \text{Na}_2\text{S} = (\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S} + 2\text{NaCl}$. The sulphur-free compounds are therefore derived from phenylthiocarbamine cyanide, but the obvious hypothesis that the next stage of the reaction occurs by a further elimination of hydrogen sulphide is negated by the observation of a similar reaction with phenylethylthiobiuret, with which this loss is impossible. It is much more probable that phenylcarbamine cyanide is produced from its thio-analogue by simple hydrolysis, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{CN} + \text{H}_2\text{O} = \text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CN} + \text{H}_2\text{S}$. The phenylcarbamine cyanide is hydrolysed in boiling alkaline solution to phenylcarbamide, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CN} + 2\text{H}_2\text{O} = \text{NHPh}\cdot\text{CO}\cdot\text{NH}_2 + \text{CO}_2 + \text{NH}_3$, and the latter is converted into the diphenyl derivative by protracted boiling of its solution. Triphenylisomelamine is derived from phenyleyanamide resulting from the desulphurisation of phenylthiocarbamide produced by the hydrolysis of phenylthiocarbamine cyanide.

The sodium salt of phenyl- ψ -thiocarbamine cyanide, $\text{C}_8\text{H}_5\text{N}_3\text{SNa}$, leaflets, is formed by the addition of phenylthiocarbimide to a cold aqueous solution of sodium cyanamide, and is converted by cautious acidification with acetic acid into *phenylthiocarbamine cyanide*, a colourless, unstable substance, m. p. (indefinite) 105° after becoming discoloured at 90° (the *silver*, *copper*, and *mercury* derivatives are described). The sodium salt is transformed by benzyl chloride into *N*-phenyl-*S*-benzyl- ψ -thiocarbamine cyanide, m. p. 189 – 190° . Under varying conditions which are described in detail in the original, the sodium salt of phenyl- ψ -thiocarbamine cyanide is converted by ethylene chlorohydrin and sodium hydroxide into *phenylcarbamine cyanide*, m. p. 123 – 124° , diphenylcarbamide, and triphenylisomelamine, the precise course of the reaction being governed largely by the amount and concentration of the alkali hydroxide. The isolation of these products from phenylthiobiuret is also described in detail. Phenylcarbamine cyanide is converted by hot, very dilute sulphuric acid into *as*-phenylbiuret, m. p. 167° . The following compounds have also been prepared: *p*-tolylcarbamine cyanide, m. p. 142° ; *p*-tolylbiuret, m. p. 199 – 200° (decomp.); *p*-phenetylcarbamine cyanide, m. p. 131° ; *o*-anisylcarbamine cyanide, decomp. 115° ; phenylethylcarbamine cyanide, $\text{NPhEt}\cdot\text{CO}\cdot\text{NH}\cdot\text{CN}$, large, colourless leaflets, m. p. 142° . H. W.

Dicyanamide. W. MADELUNG and E. KERN (*Annalen*, 1922, 427, 1–34).—The analogies suggested by cyanoform and thiocyanic acid indicate that dicyanamide should be a strong acid and although, possibly, rather unstable in the free state, quite stable in the form of its salts: $\text{HC}(\text{CN})_3$, $\text{NH}(\text{CN})_2$, $\text{HS}(\text{CN})$. The paper is devoted to a description of the preparation and properties of dicyanamide.

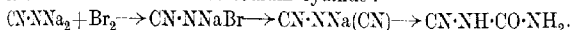
Sodium dicyanamide, $\text{NNa}(\text{CN})_2$, is obtained in good yield by treating an aqueous solution of disodium cyanamide ($\text{CN}\cdot\text{NNa}_2$) with cyanogen bromide. It is easily soluble in water, but less easily soluble in alcohol, from which it can conveniently be crystallised. Its aqueous solution is neutral to litmus. The decomposition may also be carried out by adding first cyanamide and then cyanogen bromide to an ethyl alcoholic solution of sodium ethoxide, but in these circumstances the *sodium salt of O-ethylcyanoisocarbamide* (below) is formed as a by-product, probably in the following way :



Free *dicyanamide* cannot be isolated owing to the speed with which it is converted into an insoluble amorphous polymeride of high molecular weight. However, it exists in solution long enough for it to be possible to show by conductivity measurements that it is a strong acid, nearly as strong as hydrochloric acid.

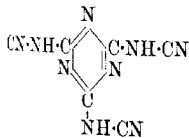
The *silver*, *cuprous*, and *mercurous* salts are colourless, the *lead*, *mercuric*, and *cupric* salts are sparingly soluble, and the *ferric* salt is soluble and red, but not so intensely coloured as ferric thiocyanate. The *ammonium* salt forms needles which melt at 116° without decomposition. The silver salt does not react with methylene iodide, but with methyl iodide it gives *dicyanomethylamide*, quadratic crystals, m. p. 221° .

Dicyanamide undergoes additive reactions with water, ammonia, and ethyl alcohol. With water in the presence of hydrochloric acid, it gives biuret, two molecules of water being taken up. The addition of one molecule of water was effected accidentally during an attempt to prepare dicyanamide from disodium cyanamide by reaction with bromine and sodium cyanide :



The product was cyanocarbamide. Addition of one molecule of ammonia is effected by heating the copper salt with concentrated aqueous ammonia. The product is a mixture of copper diguanide and cyanoguanidine, $\text{CN}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$. The compound formed by the addition of one molecule of ethyl alcohol, *O-ethylcyanoisocarbamide*, needles or prisms, m. p. 119° , is obtained either from cyanamide and cyanogen bromide as described above, or by heating sodium dicyanamide with an equivalent amount of ethyl alcoholic hydrogen chloride. If an excess of hydrogen chloride is used *O-ethylisobiuret*, m. p. 129° , is also obtained : $\text{NH}\cdot\text{C}(\text{NH})\cdot\text{OEt}$. The hydrochloride of this base readily loses ethyl chloride, giving biuret.

When sodium dicyanamide is heated to dull redness it is converted into the sodium salt of tricyanomelamine, the probable formula of which is annexed. The same compound may be obtained by heating the sodium salt of cyanoguanidine, ammonia being eliminated. Bannow obtained the potassium salt (this Journal, 1871, 391, A., 1881, 144), which he thought to be potassium dicyanamide, by heating mercuric cyanide or paracyanogen with potassium cyanide.



The sodium salt, NaC_2N_3 and $\text{NaC}_2\text{N}_3 \cdot \text{H}_2\text{O}$, is prepared by the action of fused sodamide on melon, and by heating a mixture of sodium cyanide and mercuric cyanide. The silver, magnesium, barium, cupric, and nickel salts are prepared by double decomposition of the sodium salt with a soluble salt of the metals named. A number of attempts to prepare the final de-ammonation product of this series, carbonic nitride, have only yielded very impure specimens of this compound.

J. F. S.

Crystal Structure of Potassium Cyanide. RICHARD M. BOZWORTH (*J. Amer. Chem. Soc.*, 1922, **44**, 317—323).—The crystal structure of potassium cyanide has been investigated with X-rays, making use of the Laue photographic method, the spectrometric method, and the powder method. The X-ray data show conclusively that the structure of this substance approximates closely to the sodium chloride structure. Consequently the potassium atoms were placed in the positions of the sodium atoms and the carbon and nitrogen atoms near the positions of the chlorine atoms. The positions of the carbon and nitrogen atoms which give the best agreement with the data place these atoms 1.15×10^{-8} cm. apart, equidistant from the position of the chlorine atom. The distance between the potassium and carbon atoms and the potassium and nitrogen atoms is the same, namely, 3.0×10^{-8} cm.

J. F. S.

Decomposition of Potassium Ferricyanide by the Action of Heat. V. CUTTICA (*Gazzetta*, 1922, **52**, i, 20—25).—Protracted heating of potassium ferricyanide at 230° results in complete decomposition of the salt according to the equation $2\text{K}_3\text{Fe}(\text{CN})_6 = 2\text{FeC}_2 + 2\text{N}_2 + \text{C}_2\text{N}_2 + 6\text{KCN}$. The intermediate green substance formed during the heating (cf. Locke and Edwards, A., 1899, i, 497, 557; Cuttica and Canneri, A., 1921, i, 322) exhibits the oxidising properties of the original salt, but differs from it in certain of its reactions, and contains complex iron cyanides with less than six cyanogen groups in the molecule.

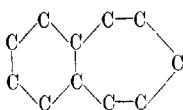
T. H. P.

Transformations during the Fission of Racemic Substances. RUDOLF WEGSCHEIDER (*Ber.*, 1922, **55**, [B], 764—766).—Pope and Peachey (P., 1900, **16**, 42, 116) have shown that in the fission of the methylethyl-*n*-propylstannic base as *d*-camphorsulphonate the salt of the *d*-base only separates so that ultimately the *l*-form is converted completely into the *d*-variety. The phenomenon has been explained by the supposition of the racemisation of the excess of *l*-salt remaining in the solution. This and similar observations are now considered from a somewhat more general theoretical point of view, and the conditions are deduced on which the transformation depends when it is due (1) to the compounds of the optical antipodes with the active reagent, and (2) to the free optical antipodes formed by dissociation. The original must be consulted for details.

H. W.

Two cycloHeptane Models Free from Strain. ERNST MOHR (*J. pr. Chem.*, 1921, [ii], **103**, 316—323).—The geometry is worked

out of two three-dimensional *cycloheptane* models which are absolutely free from strain, that is to say, two figures each with seven equal rectilinear sides are constructed so that the angle between any two sides meeting in a corner is $\alpha = \tan^{-1} \sqrt{2} =$



$109^{\circ} 28' 16''$. It is likewise possible to construct models which are free from strain for the formula annexed. These results are of interest as the heat of combustion of *cycloheptane* shows that the strains in it are practically the same as in *cyclo-*

pentane or *cyclohexane*.

W. O. K.

Dimethylcyclohexanes. G. CHAVANNE and P. BECKER (*Bull. Soc. chim. Belg.*, 1922, **31**, 95—98).—Reduction of xylenes in presence of platinum and of nickel as catalysts yields products of differing physical constants. The authors state that the substances obtained from *m*-xylene and from *p*-xylene in presence of platinum are mixtures, and that it is doubtful whether the *o*-xylene derivative is a pure substance. *o*-Xylene, in presence of nickel is transformed into a substance which is clearly distinct from that produced when platinum is used. In the case of *m*-xylene and *p*-xylene, the nature of the catalyst used affects the physical constants of the mixture obtained. The explanation put forward by the authors is based on the formation of *cis*- and *trans*-forms of stereoisomerides (cf. Skita, A., 1921, **1**, 503).

H. J. E.

The Preparation of Phenylacetylene. JOHN C. HESSLER (*J. Amer. Chem. Soc.*, 1922, **44**, 425—426).—By using molten potassium hydroxide in place of alcoholic potassium hydroxide in Nef's method (A., 1900, **i**, 20), the yield of phenylacetylene from ω -bromostyrene is increased from 60% to 80%. The α -bromostyrene is dropped on to the molten potassium hydroxide heated at 200 — 215° .

W. G.

The Monochlorotoluenes. A. WAHL, G. NORMAND, and G. VERMEYLEN (*Compt. rend.*, 1922, **174**, 946—949).—The authors have constructed the melting-point curve for mixtures of *o*- and *p*-chlorotoluenes and use this method for the determination of the relative amounts of these two isomerides formed in the chlorination of toluene under different conditions. They find that, whilst in the absence of a catalyst benzyl chloride is almost the sole product of the action of chlorine on toluene at 100° , in the presence of lead chloride the product is a mixture of the two isomeric chlorotoluenes containing about 62% of the *ortho*-isomeride.

W. G.

The Wurtz-Fittig Synthesis. WALTER FUCHS and HEINRICH METZL (*Ber.*, 1922, **55**, [B], 738—747).—The behaviour of 1:3:5- and 1:2:4-tribromobenzenes and of 3:5-dibromotoluene towards alkali metals in ethereal solution has been investigated. The two substances first named are not attacked by metallic sodium under these conditions, but react slowly with potassium or an alloy of sodium and potassium. 1:3:5-Tribromobenzene gives a mixture of substances, some of which are soluble in alkali hydroxide solution

with the formation of salts. The portion which remains undissolved is amorphous and insoluble in all media, so that its uniformity cannot be guaranteed; analysis shows the presence of oxygen in it in addition to carbon, hydrogen, and bromine, and this surprising result is confirmed by the observation that resorcinol can be obtained from it by treatment with hydriodic acid. The substances which are soluble in alkali hydroxide are precipitated in the amorphous form by the addition of acid and can be separated by sodium hydrogen carbonate into phenols and carboxylic acids. The behaviour of 1 : 2 : 4-tribromobenzene resembles that of the symmetrical isomeride, but the yields are greater; halogenated and traces of halogen-free hydrocarbons are obtained in addition to oxygen compounds.

3 : 5-Dibromotoluene reacts with sodium, giving 3 : 3'-ditolyl; the main product of the change is composed of amorphous, yellow substances to which, according to the results of analysis, the formulae, $C_{28}H_{24}Br_2$, $C_{35}H_{30}Br_2$, $C_{42}H_{36}Br_2$, $C_{56}H_{48}Br_2$ are assigned and are regarded as formed by the linear union of 4, 5, 6, or 8 toluene nuclei in such a manner that the terminal groups each contain a bromine atom, thus, $Br-C_6H_3Me-C_6H_3Me-C_6H_3Me-Br$. The formation of 3 : 3'-ditolyl is not to be explained by the reduction of the bromo-compound by hydrogen formed from adventitious moisture, since this is impossible under the experimental conditions, and, further, it is found that the yield of ditolyl is very noticeably increased when the duration of the experiment is curtailed. The most probable hypothesis is that metallic substitution products of the hydrocarbons are formed initially which contain the alkali metal in place of the bromine, for example, $Na-C_6H_3Me-C_6H_3Me-Na$. These reactive compounds can either behave in the normal manner or combine with the atmospheric oxygen to give alkali phenoxides (as with the tribromobenzenes); alternatively, as in the case of 3 : 5-dibromotoluene, they may undergo only partial intermediate decomposition and then give the corresponding hydrogen compounds after being treated with water. The formation of carboxylic acids is difficult to explain; it does not appear to be due to access of atmospheric carbon dioxide, since the relative quantities of acid and phenol remain unchanged when the gas is excluded carefully. It is possible, however, that their formation is a secondary process, since they are identified as phenol-carboxylic acids by the Schotten-Baumann reaction in alkaline solutions, which are obtained only after tedious filtrations and have thus possibly become oxidised.

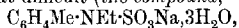
H. W.

The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. VI. The Elimination of Halogen during the Reduction of Halogenated Nitro-compounds. HAROLD BURTON and JAMES KENNER (T., 1922, 121, 673—682).

The Action of Sodium Hydrogen Sulphite on Nitro-compounds of the Benzene Series. HUGO WEIL and E. MOSER (*Ber.*, 1922, 55, [B], 732—737; cf. D.R.P. 151134).—In a large

number of cases, possibly invariably, sulphamic acids are the primary products of the reduction of benzenoid nitro-compounds with sodium hydrogen sulphite. As by-products, sulphonic acids can be obtained, which, however, are not present as such in the primary mixtures, but are formed, probably from sulposulphamic acids which are freely soluble in water, when the latter are boiled with mineral acids. Three molecules of sodium hydrogen sulphite are theoretically required for the reduction of a nitro-group, and this is found to be in practice sufficient for the purpose. Under these conditions, however, sodium hydrogen sulphate or a mixture of sulphuric acid and sodium sulphate is produced which causes the hydrolysis of the sulphamic acid; this can be avoided by the use of two additional molecular proportions of sodium hydrogen sulphite or one of normal sodium sulphite.

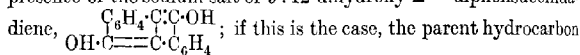
The following salts are prepared by boiling a mixture of the nitro-compound and an aqueous solution of sodium hydrogen sulphite under a reflux condenser: *sodium phenylsulphamate*, $\text{NHPh}\cdot\text{SO}_3\text{Na}\cdot 2\text{H}_2\text{O}$; *sodium p-tolylsulphamate*; *sodium o-chlorophenylsulphamate*, colourless needles ($-\text{H}_2\text{O}$); *sodium p-chlorophenylsulphamate*, colourless needles; *sodium p-phenetylsulphamate*, flattened prisms; *sodium o-anisylsulphamate* ($+1\cdot 5\text{H}_2\text{O}$); *sodium p-sulphaminobenzoate*, needles. The substances are very sensitive to acids, but remarkably resistant towards boiling solutions of alkali hydroxides. They are readily methylated by means of methyl sulphate (the *substance*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NMe}\cdot\text{SO}_3\text{Na}\cdot 1\cdot 5\text{H}_2\text{O}$, is described); on the other hand, complete ethylation with ethyl sulphate is somewhat difficult (the *compound*,



has been prepared).

H. W.

The Diphensuccindene Series. IV. 9:12-Dichloro- $\Delta^{9,11}$ -diphensuccindadiene and Diphensuccind-10-ene. K. BRAND and KARL ORTO MÜLLER (*Ber.*, 1922, 55, [B], 601–608; cf. A., 1912, i, 960; 1920, i, 486, 487).—The colour of solutions of diphensuccindandione in sodium hydroxide has been attributed to the presence of the sodium salt of 9:12-dihydroxy- $\Delta^{9,11}$ -diphensuccindadiene,



if this is the case, the parent hydrocarbon should also be coloured as a consequence of the presence of the two conjugated double bonds and of the condensed atomic grouping. Attempts to obtain the hydrocarbon are now described.

9:9:12:12-Tetrachlorodiphensuccindane, $\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CCl}_2 \\ | \\ \text{CCl}_2\cdot\text{CH}\cdot\text{C}_6\text{H}_4 \end{array}$, unstable, colourless needles, m. p. 135° (decomp.), is obtained by the action of phosphorus pentachloride on diphensuccindan-9:12-dione, and is rapidly converted by a solution of sodium acetate in alcohol

into 9:12-dichloro- $\Delta^{9,11}$ -diphensuccindadiene, $\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{C}\cdot\text{CCl} \\ | \\ \text{CCl}=\text{C}\cdot\text{C}_6\text{H}_4 \end{array}$, long,

slender, reddish-brown needles, m. p. 191° , which is obtained more conveniently by preserving a solution of the tetrachloro-compound in benzene at the atmospheric temperature. A boiling solution of

the dichloro-substance in alcohol is reduced by zinc dust in the presence of a little mercuric chloride solution to Δ^{10} -diphensuccindene, $\text{C}_6\text{H}_4\text{---C}(\text{CH}_2)_2\text{---C}_6\text{H}_4$, very pale yellow leaflets, m. p. 210° , which is trans- $\text{CH}_2\text{---C}(\text{C}_6\text{H}_4)_2\text{---CH}_2$ formed by hydrogen in the presence of palladised charcoal into diphensuccindane, $\text{C}_6\text{H}_4\text{---CH}(\text{CH}_2)_2\text{---CH}(\text{C}_6\text{H}_4)$, m. p. 102° (cf. Roser, A., 1888, 1301). Δ^{10} -Diphensuccindene is converted by benzaldehyde in the presence of alcoholic sodium ethoxide solution into a mixture of a substance, brownish-red needles or leaflets, m. p. 155° , and 9:12-dibenzylidene- Δ^{10} -diphensuccindene, $\text{C}_6\text{H}_4\text{---C}(\text{C}(\text{CHPh})_2)_2\text{---C}_6\text{H}_4$, small, cinnabar-red leaflets, m. p. 244° . The latter is reduced by hydrogen in the presence of palladised charcoal to 9:12-dibenzylidiphensuccindane, $\text{C}_6\text{H}_4\text{---CH}(\text{CH}_2\text{CH}_2\text{Ph})_2$, colourless crystals, m. p. 141° , and by zinc dust and boiling glacial acetic acid to 9:12-dibenzylidenediphensuccindane, $\text{C}_6\text{H}_4\text{---CH}(\text{C}(\text{CHPh})_2)_2\text{---C}_6\text{H}_4$, slender, colourless needles, m. p. 255° . H. W.

Constitution of Carbonium Dyes. HANS EDUARD FIERZ (*Ber.*, 1922, 55, [B], 429).—A reply to Hantzsch (this vol., i, 24). H. W.

Catalytic Preparation of Aniline. O. W. BROWN and C. O. HENKE (*J. Physical Chem.*, 1922, 26, 161—191).—The conditions under which aniline may be prepared by the reduction of nitrobenzene with hydrogen in the presence of nickel or copper as catalyst have been investigated. In the preparation of the nickel catalyst it is shown that the best temperature for the ignition of the nitrate is 450° . The oxide thus prepared is reduced to metal in the reaction furnace at about 380° by hydrogen. It is shown that merely heating the reduced nickel in hydrogen is sufficient to decrease its catalytic activity, but if it is heated to temperatures below 380° it is too active and carries the reduction too far. After heating the reduced nickel catalyst in hydrogen to a high temperature, it did not lose its activity immediately, but lost it with use, the activity decreasing almost linearly. The best temperature for the reduction of nitrobenzene to aniline with nickel as the catalyst is about 192° . The rate of flow of the hydrogen and nitrobenzene vapour through the reaction tube is of more importance than the percentage excess of hydrogen present. The best temperature for the ignition of copper nitrate for the preparation of the copper catalyst is 415° ; at lower temperatures the copper loses its activity with use and does not give as high yields as when ignited at about 415° . Heating the copper catalyst in hydrogen reduces its activity but little until the temperature exceeds 475° . Its activity is 60% lower when heated at 535° than when heated at 475° . A new copper catalyst, or one that has been oxidised

and again reduced, gains in activity with use for four to six experiments before it gives constant results. Long reduction in hydrogen increases the length of time required for it to attain its maximum activity. The best temperature for carrying out the reduction of nitrobenzene with copper as catalyst is 260° . The activity of the copper catalyst decreases when used at too high a temperature (377°). The decrease is more rapid with a more rapid rate of flow of nitrobenzene. It is further shown that with a constant rate of flow of hydrogen the lower the rate of flow of nitrobenzene the greater the yield of aniline, and with a constant rate of flow of nitrobenzene an increase in the rate of flow of the hydrogen first increases the yield of aniline and then decreases it, the increase and decrease being much more marked with copper than with nickel. The time of contact of the gaseous mixture with the catalyst is of more importance than the percentage excess of hydrogen present. It has been found that an ordinary wrought-iron pipe has considerable catalytic activity on this reaction. The activity decreases with use, and is greater when the tube has been cleaned with nitric acid before use. The activity of nickel and copper catalysts for the reduction of nitrobenzene to aniline is restored by oxidation and reduction, although not to so great an extent with copper as with nickel. As examples of the efficiency of the process, the following are quoted. (1) Nickel catalyst at 192° , 3.9 grams of nitrobenzene per hour with a 710% excess of hydrogen gives a 95.2% yield. (2) Copper catalyst at 253° , with the same quantities of hydrogen and nitrobenzene, gives a 96.2% yield of aniline.

J. F. S.

Compounds of Tellurium Tetrabromide with Organic Bases. ALEXANDER LOWY and RAYMOND F. DUNBROOK (*J. Amer. Chem. Soc.*, 1922, **44**, 614—617).—When primary, secondary, or tertiary amines or substituted amines are added to a solution of pure tellurium tetrabromide in absolute ether or glacial acetic acid, yellow or orange-coloured additive products are obtained, the following of which are described. *Dianiline tellurium tetrabromide*, $(C_6H_5 \cdot NH_2)_2TeBr_4$; *di-p-bromoaniline tellurium tetrabromide*, $(BrC_6H_4 \cdot NH_2)_2TeBr_4$; *di-diphenylamine tellurium tetrabromide*, $(NHPh_2)_2TeBr_4$; *di-dimethylaniline tellurium tetrabromide*, $(NPhMe_2)_2TeBr_4$; *di-β-naphthylamine tellurium tetrabromide*, $(C_{10}H_7 \cdot NH_2)_2TeBr_4$; *p-phenylenediamine tellurium tetrabromide*, $C_6H_4(NH_2)_2TeBr_4$; *m-tolylenediamine tellurium tetrabromide*, $C_6H_3Me(NH_2)_2TeBr_4$; *benzidine tellurium tetrabromide*, $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2 \cdot TeBr_4$; *tetramethyldiaminodiphenylmethane tellurium tetrabromide*, $NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot NMe_2 \cdot TeBr_4$.

They are all stable in air and decompose when heated at above 100° . When di-aniline tellurium tetrabromide is dissolved in dilute hydrobromic acid and recrystallised twice from the same solvent it gives a new compound, consisting of four molecules of aniline hydrobromide and one molecule of tellurium tetrabromide. The other bases form analogous products. Alkaloids such as

brucine or quinine also give yellow, amorphous precipitates with tellurium tetrabromide.

Selenium and tellurium dyes could not be obtained by substituting selenium or tellurium for sulphur in the usual method for preparing sulphur dyes. W. G.

Electrochemical Oxidation of Dimethylaniline. FR. FICHTER and EMIL ROTHENBERGER (*Helv. Chim. Acta*, 1922, 5, 166—181).—Chromic acid is unnecessary for the electrochemical oxidation of dimethylaniline to tetramethylbenzidine (cf. Löh, *Z. Elektrochem.*, 1901, 7, 608). The same result is obtained with anodes of lead dioxide, using a current density of 0.007—0.009 amp./cm.² and a solution of the base in $1\frac{1}{2}$ equivalents of 2*N*-sulphuric acid. The yield is not good, since for the best results 2—3 farads per mol. base must be used instead of 1 theoretically necessary, and carbon dioxide, nitrogen, and some carbon monoxide are evolved. Also, owing to production of formaldehyde and its condensation with unoxidised base, tetramethyldiaminodiphenylmethane is obtained. The benzidine formation is not due to a specific action of lead peroxide, since it also occurs when platinum electrodes are employed. In this case, by precipitation of the benzidine from the acid solution with barium hydroxide, an aqueous solution of a subsidiary basic product is obtained, which rapidly turns blue on exposure to air, and therefore must be concentrated in a stream of carbon dioxide under reduced pressure. The residue on distillation decomposes, sometimes explosively, into tarry products and phenyltrimethylphenylene diamine, $\text{Me}_2\text{N} \langle \bigcirc \rangle \text{NMePh}$, needles or plates, m. p. 57°. Its alcoholic or dilute mineral acid solution is easily turned blue by ferric chloride, bromine, or even atmospheric oxygen, and the base is further characterised by its perchlorate, $\text{C}_{12}\text{H}_{12}\text{N}_2 \cdot \text{HClO}_4$, blue leaflets, m. p. 186—187°; methiodide, $\text{C}_{12}\text{H}_{12}\text{N}_2 \cdot \text{MeI}$, silky leaflets, m. p. 202°, which do not give a blue colour with ferric chloride; and a nitroso-derivative, green needles, m. p. 147—149°. Attempts to synthesise this base by methylation of phenyldimethyl-*p*-phenylenediamine gave indefinite results. A small amount of this base is also formed when lead peroxide anodes are used, whilst, conversely, traces of tetramethyldiaminodiphenylmethane are formed when platinum anodes are employed. The latter are known to favour the formation of peroxides, and in the present case a small amount of the pierate of dimethylaniline oxide was obtained on treating the electrolysed solution with picric acid, after neutralisation and removal of dimethylaniline and tetramethylbenzidine. An amorphous pierate, m. p. 56—60°, obtained in much larger quantity at the same time, probably corresponds with the product which furnishes phenyltrimethyl-*p*-phenylenediamine, and is probably the oxide of *p*-dimethylaminophenol. The decomposition of this compound on distillation is probably represented by the equation $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2\text{O} + \text{NMe}_2\text{Ph} = \text{CH}_2\text{O} + \text{H}_2\text{O} + \text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMePh}$. In support of this, it is pointed out that formaldehyde and monomethylaniline are also among the

products of electrolysis. It is improbable that dimethylaniline oxide is the primary oxidation product in these reactions, since this view offers no explanation of the different results following the use of platinum and lead peroxide electrodes. When the latter are used for the oxidation of diethylaniline, tetraethylbenzidine is almost the sole product.

J. K.

Preparation of *o*-Sulphonic Acids of Aromatic Amines. BRITISH DYESTUFFS CORPORATION, LTD., JAMES BADDILEY, JOSEPH BARON PAYMAN, and HARRY WIGNALL (Brit. Pat. 175019).—Primary aromatic amines are treated with chlorosulphonic acid in presence of a suitable solvent, preferably tetrachloroethane, and the sulphonation is completed by heating. In certain cases, a chlorosulphonate separates as an intermediate product, and can, if desired, be collected by filtration and further treated in the absence of the solvent, when it is converted, with evolution of hydrogen chloride, into the sulphonic acid.

G. F. M.

The Action of Sulphuryl Chloride on Aromatic Amines. W. ELLER and L. KLEMM (*Ber.*, 1922, 55, 217–224).—By the action of sulphuryl chloride on aniline in ethereal solution in the cold, a mixture of about equal parts of 2:4:6-trichloroaniline, 2:4-dichloroaniline, and *p*-chloroaniline is obtained, the last two as hydrochlorides. The hydrochlorides are not further acted on in the cold, but at a higher temperature, for example, in boiling benzene, they are completely chlorinated to 2:4:6-trichloroaniline. Anthranilic acid in ether is chlorinated by sulphuryl chloride to a mixture of 3:5-dichloro-2-aminobenzoic acid and a monochloroanthranilic acid of m. p. 204°. This was identified as 5-chloro-2-aminobenzoic acid and corresponds with the *m*-chloro-2-aminobenzoic acid of the literature. The isomeride of m. p. 148° described in the literature as the 5-chloro-compound is actually 3-chloro-2-aminobenzoic acid. In benzene solution at 65–70°, anthranilic acid gives an 80–85% yield of 3:5-dichloro-2-aminobenzoic acid. *p*-Aminophenol reacts with sulphuryl chloride at 70° to give, besides a little chloranil, 2:3:5:6-tetrachloro-4-dichloro-amino-1-hydroxybenzene, white crystals, m. p. 71.5°, readily soluble in all organic solvents, insoluble in water and dilute hydrochloric acid, slightly soluble with a violet colour in sodium hydroxide solution, by which it is slowly decomposed.

E. H. R.

Condensation Products of Phenylhydroxylamine with Hydroxymethylene Compounds and Carbinols. II. Hydroxymethylenedeoxybenzoin and Phenylhydroxylamine. H. RUPE and R. WITTEW (Helv. Chim. Acta, 1922, 5, 205–216; cf. A., 1921, i, 425).—Interaction of hydroxymethylenedeoxybenzoin and β -phenylhydroxylamine in presence of glacial acetic acid yields acetyl trans- β -phenyl- β -(α -benzoyl)-phenylvinylhydroxylamine, CPhBz:CH·NPh·OAc, needles, m. p. 157–158°, from which trans- β -phenyl- β -(α -benzoyl)-phenylvinylhydroxylamine, CPhBz:CH·NPh·OH, needles, m. p. 166°, is obtained by careful acid hydrolysis. If sodium hydroxide be employed, β -phenyl-

β -phenylvinylhydroxylamine, $C_8H_9 \cdot CH \cdot NPhOH$, plates, m. p. 119—120°, is obtained; its synthesis from phenylhydroxylamine and ethyl hydroxymethylenephenylacetate is to be described later; its unstable dibromide easily passes into β -phenyl-bromo- β -phenylvinylhydroxylamine, $C_{14}H_{15}ONBr$, needles, m. p. 180°. *cis*- β -Phenyl- β -(α -benzoyl)-phenylvinylhydroxylamine, $C_{21}H_{17}O_2N$, needles, m. p. 158° (methyl ether, $C_{22}H_{19}O_2N$, needles, m. p. 134—135°), results if the above condensation is carried out in alcoholic solution. It is converted into its *trans*-isomeride by dilute alcoholic sulphuric acid, whilst on treatment with sodium hydroxide it furnishes benzoic acid and β -phenyl- β -1:3:4-(or -1:3:5)-triphenyl- Δ^2 -5-(or -4)-pyrrolinylhydroxylamine, $C_{28}H_{24}ON_2$, m. p. 180° (picrate, $C_{28}H_{24}ON_2 \cdot C_6H_2(NO_2)_3 \cdot OH$, m. p. 215—216°), of which the orientation is one of the two alternatives indicated. This compound, which also results from the fusion of hydroxymethylenedecoxybenzoin with β -phenylhydroxylamine, is converted by thionyl chloride into the *chloro*-derivative, $C_{28}H_{23}N_2Cl$, m. p. 216°, which is also formed when the same reagent acts on the above *cis*-derivative. None of the products now described are soluble in alkali hydroxides or possess reducing properties. *N*- α -Benzoylstyryl-*p*-aminophenol, $C_6H_5 \cdot CBz \cdot CH \cdot NH \cdot C_6H_4 \cdot OH$, lemon-yellow needles, m. p. 199—200°, is obtained by condensation of hydroxymethylenedecoxybenzoin with *p*-aminophenol in presence of acetic acid. J. K.

Condensation Products of Phenylhydroxylamine with Hydroxymethylene Compounds and Carbinols. III. Diphenylbromomethane and Phenylhydroxylamine. H. RUPE and R. WITTWER (*Helv. Chim. Acta*, 1922, 5, 217—220; cf. preceding abstract).—Diphenylcarbinol, in contrast with Michler's hydrol (A., 1921, i, 425), is unaffected by β -phenylhydroxylamine, but the reaction of the latter with diphenylbromomethane is so vigorous that decomposition ensues unless it be carried out in presence of crystallised sodium acetate. In this way, β -phenyl- β -diphenylmethylhydroxylamine (Angeli, Alessandri, and Aiazzi-Mancini, A., 1911, i, 544) is readily obtained. Its oxidation to diphenylnitron (Angeli, *loc. cit.*) is conveniently carried out in methyl alcoholic solution by means of cupric acetate. Its unimolecular formula (cf. Staudinger and Miescher, A., 1919, i, 584) is confirmed by freezing-point measurements. J. K.

Introduction of the Chloroethyl Group into Phenols, Alcohols, and Amino-compounds. GEORGE ROGER CLEMO and WILLIAM HENRY PERKIN, jun. (T., 1922, 121, 642—649).

β -Naphthol. CLARENCE E. MAY (*J. Amer. Chem. Soc.*, 1922, 44, 650—651).—In the conversion of calcium naphthalenesulphonate into the sodium salt, it is essential to use pure anhydrous sodium carbonate, free from the hydrogen carbonate. In the conversion of the sulphonate into the naphthol, the fusion must be carried out under conditions such that no oxidation can take place. For this reason iron crucibles should be avoided and commercial hydrochloric acid should not be used in the recovery of the product of the fusion. W. G.

Influence of Substituents on Reactions. VII. The Preferential Points of Substitution in the Naphthols and in α -Naphthylamine. HARTWIG FRANZEN and GUSTAV STÄUBLE (*J. pr. Chem.*, 1921, [ii], **103**, 352–390; cf. A., 1920, i, 730).—It has been previously shown (*loc. cit.*) that on brominating β -naphthylamine, 1-bromo-, 1:6-dibromo-, and 1:6:3-tribromo- β -naphthylamine are successively formed. In the case of β -naphthol, the corresponding series of bromine derivatives is obtained, only here a tetrabromo- β -naphthol can also be prepared, in which the 4-position is occupied, as well as positions 1, 6, and 3. On reduction of these brominated β -naphthols with tin, or stannous chloride and hydrochloric acid, only the bromine in the position 1 is replaced by hydrogen, whilst with sodium amalgam in alkaline solution, bromine in the 3- and 4-positions is removed, that in the 6-position resisting reduction. This stability must be due to the hydroxyl group in the β -position, as both α - and β -bromonaphthalenes are reduced to naphthalene by sodium amalgam in alkaline solution.

In the cases of α -naphthol and α -naphthylamine, the hydrogen atoms in the 2- and the 4-positions appear to be equally readily replaced by bromine, forming 2:4-dibromo-compounds, and these, on reduction with tin, or stannous chloride, and hydrochloric acid appear to lose both atoms of bromine with equal ease. 5-Bromo- α -naphthylamine is unchanged by tin and hydrochloric acid, showing that, in this respect, the effect of the α -amino-group on the 5-position is much less than on the 2- and 4-positions.

In general, the corresponding chlorine compounds are reduced with much greater difficulty, if at all. 1-Chloro- β -naphthol, 2-chloro- α -naphthol, and 2:4-dichloro- α -naphthol require the action of hydrogen iodide to eliminate the chlorine atoms, whilst even this reagent leaves 3-chloro- α -naphthol unchanged. This new compound, thin needles, m. p. 134–135°, is obtained by the reduction of 2:3:4-trichloro- α -naphthol by hydrogen iodide. If instead it is reduced by tin and hydrochloric acid, a substance which is apparently a mixture of mono- and di-chloro- α -naphthol is obtained. α - and β -Chloronaphthalenes are not changed by the action of sodium amalgam.

Alcoholic potash is without action in 1:6-dibromo- β -naphthol, whilst it removes bromine from 2:4-dibromo- α -naphthol, although no definite product has been isolated.

The following new compounds are described in the paper. 1-Bromo-2-methoxynaphthalene, colourless plates with a nacreous lustre, m. p. 85°; 1:6-dibromo-2-methoxynaphthalene, lustrous, colourless leaflets, m. p. 102°; 6-bromo-2-methoxynaphthalene, small, colourless needles, m. p. 108°; 3:6-dibromo-2-methoxynaphthalene, fine, colourless needles, m. p. 103°; 3:6-dibromo-2-acetoxynaphthalene, brown, compact crystals, m. p. 128°; 3:6-dibromo-2-benzoxynaphthalene, fine, colourless needles, m. p. 128–129°; 1-chloro-2-methoxynaphthalene, pale yellow prisms, m. p. 70–71°; 3:6-dibromo-1-nitro- β -naphthol, fine, yellow needles, m. p. 147° (decomp.), obtained by the action of sodium nitrite and acetic acid on 1:3:6-tribromo- β -naphthol (and also by nitrating 3:6-dibromo- β -naphthol, fine, colourless needles, m. p. 134–135°);

1:3:4:6-tetrabromo-2-methoxynaphthalene, fine, colourless, felted needles, m. p. 149°; 3:4:6-tribromo- β -naphthol, colourless needles, m. p. 127—128°; 6-bromo- β -naphthol, small, colourless needles, m. p. 128°.

2:6-Dichloronaphthalene, when pure, melts at 140—141°, not 135° as given in the literature. W. O. K.

Tautomerism of Phenols. V. 1:5- and 2:7-Dihydroxynaphthalenes. WALTER FUCHS and WALTER STIX (*Ber.*, 1922, 55, [B], 658—670; cf. A., 1921, i, 241).—The occurrence of tautomerism with the two dihydroxynaphthalenes has been demonstrated.

1:5-Dihydroxynaphthalene is heated on the water-bath for about thirty days with a freshly prepared, concentrated solution of sodium hydrogen sulphite which contains rather more than two equivalents of the latter, whereby the sodium salt, $C_{10}H_{10}O_5S_2Na_2$, is obtained as a yellow, crystalline powder. It readily loses one molecular proportion of sodium hydrogen sulphite when treated with alkali hydroxide or when boiled with water, giving sodium 5-hydroxy-

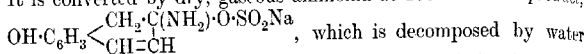
1-ketotetrahydronaphthalene-3-sulphonate, $OH \cdot C_6H_3 < \begin{matrix} CO-CH_2 \\ CH_2-CH-SO_3Na \end{matrix}$,

from which sulphur dioxide is not removed by protracted treatment with boiling acids or alkalis, and only to a small extent by hot barium chloride and hydrogen peroxide. It is not affected by a solution of bromine in anhydrous chloroform. The constitution of the substance is deduced from the observation that it is convertible into a phenylhydrazone, $C_{16}H_{16}O_4N_2S$, colourless crystals, m. p. 203° (decomp.) (the alkali, barium, calcium, copper, and lead salts were examined), from which the original ketone can be regenerated by treatment with benzaldehyde; the methyl ether of the phenylhydrazone was also prepared. Further, it is converted by diazomethane into sodium 5-methoxy-1-ketotetrahydronaphthalene-3-sulphonate, $C_{11}H_{11}O_5SNa$, an almost colourless, crystalline substance. Oxidation of either methyl ether with permanganate appears to yield 3-methoxyphthalic acid. It thus appears to be established that the product of the action of sodium hydrogen sulphite on 1:5-dihydroxynaphthalene

must have the constitution $OH \cdot C_6H_3 < \begin{matrix} C(OH)(O \cdot SO_2Na) \cdot CH_2 \\ CH(SO_3Na) \end{matrix} \text{---} CH_2$ or $OH \cdot C_6H_3 < \begin{matrix} C(OH)(O \cdot SO_2Na) \cdot CH_2 \\ CH_2 \end{matrix} \text{---} CH-SO_3Na$. The latter conception is preferred, mainly because the substance does not exhibit any tendency to involve the hydroxyl group in position 5 in the formation of a sulphone.

Under analogous conditions, 2:7-dihydroxynaphthalene behaves in a very different manner towards sodium hydrogen sulphite solution, giving a crystalline product, $C_{10}H_9O_3SNa$, in only 20% yield. The new substance is somewhat unstable and is noticeably decomposed by solution in water. It appears to have the constitution $OH \cdot C_6H_3 < \begin{matrix} CH_2 \cdot C(OH) \cdot O \cdot SO_2Na \\ CH=CH \end{matrix}$. This conception is sup-

ported by the observation that it readily decolorises the solution of a molecular proportion of bromine in dry chloroform without liberation of any considerable quantity of hydrogen bromide, but it was not possible to isolate a bromodihydroxynaphthalene from the product. The ketone-bisulphite likewise reacts with phenylhydrazine, but this reaction will be fully described subsequently. It is converted by dry, gaseous ammonia at 100° into the product,



with the formation of 7-amino- β -naphthol (acetyl derivative, m. p. 232°).

The mechanism of Bucherer's reaction is probably as follows. The naphthol, functioning in its tautomeric form, unites with the hydrogen sulphite to give a carbonyl-bisulphite compound; the hydroxyl group of this can be replaced by the amino-group, giving an intermediate product containing nitrogen and sulphur (see above), which is ultimately transformed into the amino-compound.

H. W.

Pyrogallol 1:3-Dimethyl Ether. I. K. BRAND and H. COLLISCHONN (*J. pr. Chem.*, 1921, [ii], **103**, 329—351).—On attempting to acetylate pyrogallol 1:3-dimethyl ether with acetic anhydride in presence of a few drops of concentrated sulphuric acid, 3-acetoxy-2:4-dimethoxyacetophenone, colourless leaflets, m. p. 110 — 111° , is obtained. This forms a phenylhydrazone, $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_2$, yellow crystals, which are unstable in the air, m. p. 107 — 108° , and with hydroxylamine it loses an acetyl group to form 3-hydroxy-2:4-dimethoxyacetophenone oxime, colourless crystals, m. p. 112° . Similarly, with benzaldehyde and alkali 3-hydroxy-2:4-dimethoxy-phenyl styryl ketone, m. p. 78° , is formed which with a solution of bromine in ether yields a dibromide, m. p. 147 — 150° (decomp.). The ketone, on methylation, gives 2:3:4-trimethoxyphenyl styryl ketone, yellow crystals, m. p. 71 — 72° , and this on oxidation yields 2:3:4-trimethoxybenzoic acid, m. p. 99° , which proves the position of the ketonic group. 3-Acetoxy-2:4-dimethoxyacetophenone on hydrolysis yields 3-hydroxy-2:4-dimethoxyacetophenone, colourless crystals, m. p. 79 — 80° , which forms a phenylhydrazone, m. p. 108 — 110° , and on methylation gives 2:3:4-trimethoxyacetophenone, m. p. 15 — 17° .

On boiling pyrogallol 1:3-dimethyl ether with acetic anhydride, the simple acetyl derivative is obtained, m. p. 53 — 5° , which when nitrated gives 4-nitro-2-acetylpyrogallol 1:3-dimethyl ether, yellowish-red crystals, m. p. 92 — 93° . On hydrolysis, this yields 4-nitropyrogallol 1:3-dimethyl ether, $\text{C}_8\text{H}_9\text{O}_5\text{N} \cdot \text{H}_2\text{O}$, long, thin, yellow needles, m. p. 67 — 68° , and this on methylation gives 4-nitropyrogallol trimethyl ether, m. p. 44° , described by Einhorn, Cobliner, and Pfeiffer (*A.*, 1904, i, 238), which proves the position of the nitro-group. 4-Nitro-2-acetylpyrogallol 1:3-dimethyl ether, on electrochemical reduction, yields 4-amino-2-acetylpyrogallol 1:3-dimethyl ether, which is unstable; its hydrochloride is pure white, m. p. 210° (decomp.). On diazotisation and coupling with β -naphthol, a red

azo-compound is produced, forming metallic, lustrous needles, m. p. 165—166°. The amino-compound forms an *acetyl* derivative, colourless leaflets, m. p. 131—132°, and a *benzoyl* derivative, m. p. 150—151°. On further nitration, 4 : 6-dinitro-2-acetylpyrogallol 1 : 3-dimethyl ether, yellow crystals, m. p. 127—128°, is formed, and this on hydrolysis yields 4 : 6-dinitropyrogallol 1 : 3-dimethyl ether, yellow needles, m. p. 162—163°, which on methylation gives 4 : 6-dinitropyrogallol trimethyl ether, m. p. 87—88°, described by Thoms and Siebeling (A., 1911, i, 724). W. O. K.

The Action of Benzoyl Peroxide on Cholesterol. A. WINDAUS and H. LÜDERS (*Z. physiol. Chem.*, 1921, 115, 257—269).—The authors have previously directed attention to the fact that the so-called metacholesterol described by Lifschütz (A., 1919, i, 591; 1920, i, 547) is only an impure cholesterol as prepared from cholesterol dibromide (A., 1920, i, 675). They now show further that the action of benzoyl peroxide on cholesterol does not, as claimed by Lifschütz (*loc. cit.*), produce metacholesterol but a mixture of unchanged cholesterol and cholestan-4 : 7-diol monobenzoate.

By the prolonged action of benzoyl peroxide on cholesterol in ethyl alcohol, a product is obtained which has m. p. 106—110°. With acetic anhydride, it gives a more than 50% yield of cholesteryl acetate. Similarly, a 60% yield of cholesterol dibromide can be obtained from the product. Finally, after precipitating the cholesterol from the mixture as its digitonide they have isolated from the residue cholestan-4 : 7-diol 7-monobenzoate, m. p. 186°, which was identified by preparing its acetyl derivative, m. p. 154°, and the dibenzoate, m. p. 212°. Further identification was obtained by saponifying the benzoate and oxidising the diol.

The product, therefore, of the action of benzoyl peroxide on cholesterol is either an isomorphous mixture of cholesterol and cholestan-4 : 7-diol monobenzoate or a loose compound of these two substances. W. G.

New Hydroxamic Acids derived from cycloPropanecarboxylic Acid, isoButyric Acid, and Dibenzylacetic Acid. A Comparative Study of the Beckmann Rearrangement of their Derivatives. LAUDER WILLIAM JONES and ALFRED W. SCOTT (*J. Amer. Chem. Soc.*, 1922, 44, 407—423; cf. this vol., i, 248).—The hydroxamic acids described were prepared with the view of studying the influence of certain hydrocarbon radicles on the ease of rearrangement of the related hydroxamic acids. The sodium, potassium, and silver salts of the acetyl and benzoyl esters of the parent hydroxamic acids were used for comparison. The ease of rearrangement of these salts is given by the order $K > Na > Ag$. Similarly, the comparative influence of the various hydrocarbon radicles studied is given by the order $\text{dibenzylmethyl} > \text{isopropyl} > \text{benzylmethyl} > \text{cyclopropyl}$.

cycloPropanecarboxylhydroxamic acid, $\begin{matrix} \text{H}_2\text{C} \\ | \\ \text{H}_2\text{C} \end{matrix} > \text{CH} \cdot \text{CO} \cdot \text{NH} \cdot \text{OH}$, m. p. 124° (decomp.), is obtained by the action of hydroxylamine hydrochloride on ethyl cyclopropanecarboxylate in the presence of

sodium methoxide. It yields a *benzoyl ester*, m. p. 150°, with its *potassium, sodium, and silver salts*. The *acetyl ester*, m. p. 108°, gives a *potassium salt*. Both these potassium salts decompose spontaneously when kept in a vacuum desiccator over sulphuric acid.

Dibenzylacetic acid reacts with thionyl chloride to give *dibenzylacetyl chloride*, b. p. 203–205°/17 mm., which with hydroxylamine hydrochloride and sodium methoxide yields *dibenzylacethydroxamic acid*, m. p. 146°. A better yield is obtained by the action of hydroxylamine itself on the acid chloride in dry benzene. From the hydroxamic acid can be prepared its *benzoyl ester*, m. p. 147°, giving a *silver salt*; and its *acetyl ester*, m. p. 126°, giving a *silver salt*. In neither case can the potassium and sodium salts be isolated owing to the ease with which they undergo rearrangement. The product of rearrangement in the presence of water is *s-bisdibenzylmethylcarbamide*, $\text{CO}[\text{NH}\cdot\text{CH}(\text{CH}_2\text{Ph})_2]_2$, m. p. 159°.

Attempts were made to prepare tribenzylacethydroxamic acid, but they were not successful. *Tribenzylmethyl chloride*, m. p. 173° (decomp.), was obtained by the action of acetyl chloride on tribenzylcarbinol. Attempts to prepare a Grignard reagent from it by the action of magnesium even in the presence of starters were not successful.

isobutyrylhydroxamic acid (dimethylacethydroxamic acid), m. p. 116°, was prepared either by the action of hydroxylamine hydrochloride on ethyl isobutyrate in the presence of sodium methoxide or by the interaction of isobutyryl chloride and hydroxylamine in dry benzene. It yields a *benzoyl ester*, m. p. 148°, giving *potassium, sodium, and silver salts*, and an *acetyl ester*, m. p. 87°, giving a *potassium salt*.
W. G.

The Constitution of the Secondary Product in the Sulphonation of Cinnamic Acid. F. J. MOORE and RUTH THOMAS (*J. Amer. Chem. Soc.*, 1922, **44**, 367–369).—Contrary to the statement of Beilstein (*Handbuch org. Chem.*, 3 ed., **2**, 1422), it is shown that the second product obtained by Rudnew (cf. *A.*, 1875, 76) in the sulphonation of cinnamic acid is *m*-sulphocinnamic acid, and that it is identical with that obtained by Kafka (cf. *A.*, 1891, 720) from *m*-sulphobenzaldehyde by the Perkin synthesis. It may readily be characterised by its *aniline hydrogen salt*, m. p. 238°.
W. G.

Ring-chain Tautomerism. I. The Occurrence and Effect of Keto-enol Tautomerism between a Ring Compound and its Open-chain Isomeride. GEORGE ARMAND ROBERT KON, ARNOLD STEVENSON, and JOCELYN FIELD THORPE (*T.*, 1922, 121, 650–665).

Preparation of Phthalic Anhydride by the Catalysis of the Vapour Phase Reaction between Naphthalene and Atmospheric Air. COURTNEY CONOVER and H. D. GIBBS (*J. Ind. Eng. Chem.*, 1922, **14**, 120–125).—Naphthalene is oxidised to phthalic anhydride when a mixture of naphthalene vapour and air is passed through a heated tube containing certain catalysts. Vanadium pentoxide is the best catalyst for the purpose; at

about 400°, 55% of the naphthalene is oxidised, 27% may be recovered and 18% is lost, the yield of phthalic anhydride being 87% of the naphthalene attacked. Molybdenum trioxide is also a fairly efficient catalyst, but other metallic oxides tried and even finely divided platinum mixed with magnesia are poor or worthless. Fused and powdered vanadium pentoxide is more effective than is the light powder prepared by decomposing ammonium vanadate at low temperatures. Arsenic trioxide and sulphur dioxide do not interfere with the catalyst, but the presence of sodium compounds is injurious. Phthalic anhydride is the main solid product of the reaction; benzoic acid has been found, and naphthols are probably present in small quantity. The gaseous products consist chiefly of carbon dioxide; the presence of carbon monoxide has not been detected.

W. P. S.

Friedel and Crafts' Reaction. Diphenyl and Ditolyl Tetrahalogen Phthalides. WALTER A. LAWRENCE and HAROLD G. ODDY (*J. Amer. Chem. Soc.*, 1922, **44**, 329—330).—The method used by Rubidge and Qua for the preparation of diphenylphthalide (cf. A., 1914, i, 539) gives good results for the preparation of diphenyl- and ditolyl-tetrahalogenophthalides if tetrahalogenated phthalic anhydrides are used. New compounds prepared by this method are: *diphenyltetrabromophthalide*, m. p. 202°; *ditolyltetrabromophthalide*, m. p. 196—197°; *diphenyltetraiodophthalide*, m. p. 206°, and *ditolyltetraiodophthalide*, m. p. 213—214°.

W. G.

Mechanism of the Colour Change of some Phthaleins. A. THIEL (*Z. physikal. Chem.*, 1922, **100**, 479—488).—The author has investigated the colour changes of various chloro- and bromo-substituted phenolphthaleins and from the relative intensity of the colour discusses the mechanism of the colour change. Taking the intensity of the colour of phenolphthalein itself as unity, the following intensity values have been obtained: Phenoltetrachlorophthalein, 5; chlorophenolphthalein, 0.65; dichlorophenolphthalein, 0.25; trichlorophenolphthalein, 0.13; tetrachlorophenolphthalein, 0.01; bromophenolphthalein, 0.60; dibromophenolphthalein, 0.20; tribromophenolphthalein, 0.04, and tetrabromophenolphthalein, 0.01. The results show that the nuclear ring has no chromophoric function and that this must be sought outside the nucleus. The sensitiveness towards large excess of strong bases is practically zero in the case of phenoltetrachlorophthalein; it is noticeable with phenolphthalein and increases with increasing number of chlorine or bromine atoms in the side rings, so that under similar conditions the tetra-derivatives show the strongest decoloration by alkali hydroxides. The decolorising action of alcohol is parallel with that of alkali hydroxides; cooling reduces the colour intensity and heating increases it.

J. F. S.

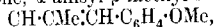
The Molecular Configurations of Polynuclear Aromatic Compounds. I. The Resolution of γ -6:6'-Dinitro- and 4:6:4':6'-Tetranitro-diphenic Acids into Optically Active Components. GEORGE HALLATT CHRISTIE and JAMES KENNER (*T.*, 1922, **121**, 614—620).

Disalicylic or Anhydrosalicylic Acid and its Transformation into Xanthone-4-carboxylic Acid. RICHARD ANSCHÜTZ and WALTER CLAASEN (*Ber.*, 1922, 55, [B], 680—689; cf. A., 1920, i, 48).—*o*-Tolylsalicylic acid, $C_6H_4Me \cdot O \cdot C_6H_4 \cdot CO_2H$, m. p. 133.5° , is prepared according to the directions of Ullmann and Zlokasoff (A., 1905, i, 597) and is oxidised by potassium permanganate to *disalicylic acid* [*anhydrosalicylic acid*], $O(C_6H_4 \cdot CO_2H)_2$, colourless needles, m. p. 230° (decomp.); the *silver*, *calcium* ($+H_2O$), and *copper* salts are described. The acid is converted by phosphorus pentachloride in the presence of *s*-tetrachloroethane into the corresponding *chloride*, $O(C_6H_4 \cdot COCl)_2$, small, colourless needles, m. p. 161° , from which the following compounds are obtained in the usual manner: *ethyl ester*, b. p. $220^\circ/12$ mm.; *di-amide*, small, colourless needles, m. p. 265° ; *di-anilide*, four-sided, lustrous leaflets, m. p. 194 — 195° . *Methyl disalicylate*, prepared by the action of methyl sulphate and potassium hydroxide on the acid, crystallises in small, colourless needles, m. p. 65.5° .

Disalicylic acid shows a somewhat unexpected behaviour towards acetyl chloride at 170° , since, in place of the expected anhydride, it gives *xanthone-4-carboxylic acid*, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix} C_6H_3 \cdot CO_2H$ (the same compound is produced by means of sulphuric acid); it crystallises in almost colourless, matted needles, m. p. 289° , and is characterised by unusual stability, since it can be distilled unchanged under the atmospheric pressure. The *silver*, *calcium*, and *copper* ($+H_2O$) salts are described. The acid is characterised further by conversion into the following derivatives; *chloride* (by phosphorus pentachloride or thionyl chloride), m. p. 165° ; *methyl ester* (by means of methyl sulphate), long, yellow needles, m. p. 146.5° ; *ethyl ester* (from the silver salt and ethyl iodide), microscopic yellow needles, m. p. 123° ; *amide* (from the chloride and ammonia in *s*-tetrachloroethane solution), m. p. above 320° (decomp.); *anilide*, colourless, lustrous leaflets, m. p. 252° .

H. W.

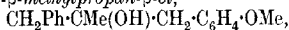
Some Derivatives of Anisylacetone (Methoxyphenylpropanone) [*p*-Methoxybenzyl Methyl Ketone]. EMILIEN LE BRAZIDEC (*Bull. Soc. chim.*, 1922, [iv], 31, 255—265).—*p*-Methoxybenzyl methyl ketone is converted by the action of hydrobromic acid in solution in glacial acetic acid into *p-hydroxybenzyl methyl ketone*, $OMe \cdot CH_2 \cdot C_6H_4 \cdot OH$, m. p. 35.5° , d^{20}_D 1.1159, giving a *semicarbazone*, m. p. 213° . With potassium cyanide, the bisulphite compound of anisylacetone yields *α -hydroxy- β -anisyl- α -methylpropionitrile*, $OMe \cdot C_6H_4 \cdot CH_2 \cdot CMe(OH) \cdot CN$, which on hydrolysis gives first the *amide*, m. p. 179° , and then *α -hydroxy- β -anisyl- α -methylpropionic acid*, m. p. 84° . By the action of magnesium methyl iodide on anisylacetone, *α -anisyl- β -methyl- Δ^a -propene*,



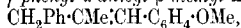
b. p. $118^\circ/15$ mm., d 1.0089, is obtained, but its properties do not entirely correspond with those given by Klages (cf. A., 1904, i, 567) for a compound thus named and prepared from anisaldehyde and

sodium isobutyrate. Its constitution is shown by the fact that on oxidation it yields anisic acid. On reduction by sodium in absolute alcohol, it gives α -anisyl- β -methylpropane, b. p. 123—125°/15 mm., d_4^{20} 0.9887.

By the action of magnesium benzyl chloride on anisylacetone, γ -phenyl- α -anisyl- β -methylpropan- β -ol,



b. p. 225—230°/15 mm., is obtained, and on dehydration by acetic anhydride it yields γ -phenyl- α -anisyl- β -methyl- Δ^{α} -propene,

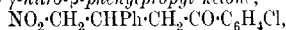


b. p. 206°/12 mm., d_4^{20} 1.0551, and this on oxidation gives anisic acid. W. G.

The Synthesis of Aromatic Ketones by means of Mixed Zinc Organic Compounds. F. MAUTHNER (*J. pr. Chem.*, 1921, [ii], 103, 391—396).—Following Blaise (A., 1911, i, 415), the author has prepared various aromatic ketones by the action of mixed zinc organic compounds on the corresponding acid chlorides. From *o*-toluoyl chloride is obtained *o*-tolyl ethyl ketone, an oil, b. p. 219—220°. The following compounds are also described: *m*-tolyl methyl ketone, an oil, b. p. 220°; *p*-tolyl ethyl ketone, an oil, b. p. 238—239°; 2-methoxy-*m*-toluoyl chloride, b. p. 121—122°/17 mm.; 2-methoxy-*m*-tolyl ethyl ketone, b. p. 122°/12 mm.; 2-methoxy-*p*-toluoyl chloride, b. p. 153—154°/18 mm.; 2-methoxy-*p*-tolyl ethyl ketone, b. p. 147°/14 mm.; 4-methoxy-*m*-toluoyl chloride, b. p. 146—147°/14 mm.; 4-methoxy-*m*-tolyl ethyl ketone, b. p. 142—143°/13 mm.; *p*-anisyl methyl ketone, and 3:5-dimethoxyphenyl ethyl ketone, b. p. 168—170°/17 mm. The last compound, when reduced with zinc and hydrochloric acid, yields 3:5-dimethoxy-1-*n*-propylbenzene. If the formula proposed by Hesse (A., 1911, i, 208) for divarinol is correct, this compound ought to be identical with divarinol dimethyl ether. W. O. K.

The Reaction between Alkalis and certain Nitrocyclopropane Derivatives. E. P. KOHLER and L. I. SMITH (*J. Amer. Chem. Soc.*, 1922, 44, 624—634).—It has previously been shown (A., 1919, i, 582) that 3-nitro-2-benzoyl-1-phenylcyclopropane is decomposed by potassium hydroxide, giving potassium nitrite and an open-chain β -diketone. It is suggested that the first step in this reaction is the elimination of nitrous acid and then the resulting cyclopropene derivative immediately undergoes rearrangement to an acetylenic compound which in the presence of the alkali hydroxide combines with water to give the β -diketone. Certain experimental evidence in support of this view is given. Proof of the intermediate formation of an acetylenic ketone was obtained by carrying out the reaction in the presence of diethyl malonate, when α -pyrone esters were obtained (cf., this vol., i, 461).

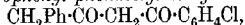
p-Chlorophenyl γ -nitro- β -phenylpropyl ketone,



m. p. 80°, is obtained by the action of sodium nitromethane on *p*-chlorophenyl styryl ketone. When brominated, it yields *p*-chlorophenyl α -bromo- γ -nitro- β -phenylpropyl ketone, m. p. 88—89°, which

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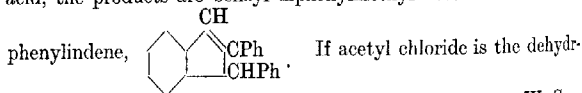
by the elimination of hydrogen bromide with potassium acetate gives 3-nitro-1-p-chlorobenzoyl-2-phenylcyclopropane, m. p. 121°. This compound is converted into an isomeride, m. p. 144°, by the action of ammonia in methyl alcohol. Further, it combines with hydrogen bromide, giving p-chlorophenyl γ -bromo- β -nitro- γ -phenylpropyl ketone, $\text{CHPhBr}\cdot\text{CH}(\text{NO}_2)\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Cl}$, m. p. 123°, which readily loses nitrous acid and hydrogen bromide, giving 1-phenyl-4-p-chlorophenylfuran, m. p. 123°. The nitrocyclopropane described above is decomposed by sodium methoxide, giving as its sole product p-chlorophenyl phenacetylmethyl ketone,



m. p. 78°, giving a copper derivative, m. p. 218—220° (decomp.). If the nitrocyclopropane is warmed with the sodium derivative of diethyl malonate in methyl alcohol, then the product is methyl 5-p-chlorophenyl-3-benzylpyrone-2-carboxylate, m. p. 171°, giving the free acid, m. p. 155—157° (decomp.), and some γ -p-chlorobenzoyl- β -benzylcrotonic acid, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_2\text{Ph})\cdot\text{CH}\cdot\text{CO}_2\text{H}$, m. p. 147° (decomp.). The pyrone acid, when heated at 165—170°, gives 6-p-chlorophenyl-4-benzylpyrone, m. p. 167—168°. The pyrone ester when shaken with a saturated solution of ammonia in methyl alcohol gives ethyl 2-hydroxy-6-p-chlorophenyl-4-benzylpyridine-3-carboxylate, m. p. 210°.

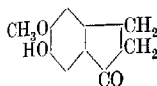
Starting from phenyl p-chlorostyryl ketone, a similar series of compounds can be prepared as follows. Phenyl γ -nitro- β -p-chlorophenylpropyl ketone, m. p. 96°; phenyl α -bromo- γ -nitro- β -p-chlorophenylpropyl ketone, m. p. 116°; 3-nitro-1-benzoyl-2-p-chlorophenylcyclopropane, m. p. 66—67°, and its isomeride, m. p. 157—159°; phenyl γ -bromo- β -nitro- γ -p-chlorophenylpropyl ketone, m. p. 112—114°; phenyl β -nitro- γ -hydroxy- γ -p-chlorophenylpropyl ketone, m. p. 142°; phenyl p-chlorophenylacetylmethyl ketone, m. p. 52—54°, and its copper derivative, m. p. 229—230° (decomp.); methyl 3-p-chlorobenzyl-5-phenylpyrone-2-carboxylate; phenyl α -dibromo- β -nitro- γ -p-chlorophenylpropyl ketone, m. p. 143°. W. G.

The Dehydration of Benzylhydrobenzoin ($\alpha\beta$ -Triphenylpropane- $\alpha\beta$ -diol). Formation of Benzyl Diphenylmethyl Ketone (Semipinacolic Transposition) and of Diphenylindene (Cyclisation). A. ORÉKHOFF and M. TIFFENEAU (*Bull. Soc. chim.*, 1922, [iv], 31, 253—255).—It has previously been shown that $\alpha\beta$ -triphenylpropane- $\alpha\beta$ -diol is dehydrated by concentrated sulphuric acid, giving benzyl diphenylmethyl ketone (A., 1919, i, 205). It is now shown that if phosphoric oxide is used in place of sulphuric acid, the products are benzyl diphenylmethyl ketone and 1:2-di-



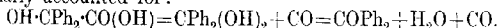
Hydrindones. I. The Hydrindone of the Vanillin Series. FRITZ VON KONEK and NIKOLAUS SZAMÁK (*Ber.*, 1922, 55, 102—109).—The object of the research was to determine the influence

of a third ring substituent on the condensation to hydroxyhydrindones of suitable phenolic acids. Hydroferulic acid (β -*m*-methoxy-*p*-hydroxyphenylpropionic acid), was prepared by reducing ferulic acid with sodium amalgam, the ferulic acid being obtained from vanillin by Perkin's synthesis. The hydroferulic acid was condensed by heating with concentrated sulphuric acid at 140° . The resulting hydrindone, which was obtained in poor yield, crystallises from hot water in long needles, m. p. $193-194^\circ$. It forms a *phenylhydrazone*, m. p. $205-210^\circ$ (decomp.), crystallising in yellow needles. By methylation and oxidation with nitric acid, it is converted into *m*-hemipinic acid (4:5-dimethoxyphthalic acid), which establishes the constitution of the hydrindone as 6-hydroxy-5-methoxydihydrindone (annexed formula). Condensation therefore takes place in the position para to the methoxyl group.



E. H. R.

The Rearrangement of Benzil to Benzilic Acid. ARTHUR LACHMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 330-340).—By prolonged boiling with water, benzil is converted into benzilic acid. The addition of small amounts of alkali accelerates the change, but the acceleration is by no means proportional to the increase in hydroxyl-ion concentration. There is some slight experimental evidence that the reversal of the benzil rearrangement is not unlikely, but so far it has not definitely been accomplished. When boiled with water, benzilic acid yields benzophenone and carbon monoxide. The author is of the opinion that the new experimental evidence is not in accord with the hypotheses of Nef (cf. *A.*, 1898, i, 102), Tiffeneau (cf. *A.*, 1907, i, 304, 404, 922), or Michael (cf. *A.*, 1920, i, 417, 536) as to this rearrangement. He propounds a new hypothesis similar to that suggested for the rearrangement of dihydroxytartaric acid (cf. this vol., i, 109), that is to say, on the basis of intramolecular oxidation and reduction. The rearrangement is indicated as follows, $\text{COPh}\cdot\text{COPh} \rightarrow \text{CPh}(\text{OH})_2\cdot\text{CPh}(\text{OH})_2 \rightarrow \text{OH}\cdot\text{CPh}_2\cdot\text{C}(\text{OH})_3 \rightarrow \text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$. The decomposition of benzilic acid to benzophenone and carbon monoxide may be similarly accounted for:



From a study of this and other rearrangements, it is stated that if two carbon atoms in a compound are in a symmetrical or a similar state of oxidation, such a structure is unstable; one of the carbon atoms tends to a greater degree of oxidation, the other becoming reduced. This tendency is enhanced by rise in temperature or by different catalysts.

W. G.

Piperitone. II. Benzylidene-*dl*-piperitone. JOHN READ and HENRY GEORGE SMITH (*T.*, 1922, **121**, 574-582).

Piperitone. III. The Oximes of *dl*-Piperitone. JOHN READ, HENRY GEORGE SMITH, and MARIE BENTIVOGLIO (*T.*, 1922, **121**, 582-593).

New Halogen Derivatives of Camphor. II. α' -Bromo-camphor. THOMAS MARTIN LOWRY, VICTOR STEELE, and HENRY BURGESS (T., 1922, 121, 633—641).

New Distinctive Characteristics of the Three Propan- β -olcamphorcarboxylolides Melting Respectively at 141°, 117—118°, and 89—90°. A. HALLER and (MME) RAMART-LUCAS (Compt. rend., 1922, 174, 785—789; cf. A., 1921, i, 673).—With sodium ethoxide the camphorcarboxylolide, m. p. 141°, gives

propan- β -olcamphorcarboxylic acid, C_8H_{14} $\begin{matrix} \diagup \\ C \\ \diagdown \end{matrix}$ $\begin{matrix} (CO_2H) \cdot CH_2 \cdot CHMe \cdot OH, \\ CO \end{matrix}$ m. p. 160—170° (decomp.), $[\alpha]_D + 33^\circ 5'$, which when heated loses carbon dioxide, giving camphopropan- β -ol. The acid is the *cis-trans*-acid. The camphorcarboxylolide, m. p. 117—118°, under the same conditions gives the *sodium salt* of an isomeric *cis-cis-propan- β -olcamphorcarboxylic acid*. Attempts to isolate the free acid were not successful as the addition of acid to a solution of the sodium salt always regenerated the olide. The third camphor carboxylolide, m. p. 89—90°, can be obtained in small amounts by treating the isomeride, m. p. 141°, with concentrated sulphuric acid. When treated with sodium ethoxide as described above, it gives an isomeric *propan- β -olcamphorcarboxylic acid*, m. p. 115—120° (decomp.), $[\alpha]_D + 25^\circ 3'$, which when heated loses carbon dioxide, giving a *camphopropan- β -ol*, m. p. 100—101°, $[\alpha]_D + 62^\circ 4'$, which yields a *phenylurethane*, m. p. 120—120.5°, $[\alpha]_D + 5^\circ 47'$. W. G.

Various Oils of *Origanum vulgare* from Different Parts of Italy. E. ANGELESCU (Gazzetta, 1922, 52, i, 157—166).—Three samples of *Origanum vulgare*, (1) one purchased in Rome, and the others gathered (2) at Valle d'Inferno and (3) in Sicily, respectively, have been distilled in a current of steam, the whole plant being employed. The yields of oil obtained were 0.204, 0.072, and 1.106%, respectively, and the compositions as follows: (1) 6.7% of thymol, 15.4% of unidentified free alcohols, 2.63% of esters, a small proportion of free acid, and 12.5% of a sesquiterpene, b. p. 245—250°, the density and refraction of which indicate it to be bicyclic; (2) 2.2% of thymol, 12.86% of unidentified free alcohols, 2.56% of esters, and probably a sesquiterpene; (3) 50% of thymol, 4% of unidentified free alcohols, 0.85% of esters, traces of free acid, 17.5% of cymene, and 10.5% of dipentene. [Cf. J. Soc. Chem. Ind., 1922, 346A.] T. H. P.

Italian Oil of *Thymus striatus*. P. LEONE and E. ANGELESCU (Gazzetta, 1922, 52, i, 152—157).—The dried complete plant yields 0.342% of a lemon-yellow oil of aromatic odour and burning taste and containing 30% of thymol, 9.5% of unidentified free alcohols, 2.83% of esters, little free acid, 29% of cymene, and 4.5% of a sesquiterpene, b. p. 250—260°, which is apparently monocyclic. [Cf. J. Soc. Chem. Ind., 1922, 346A.] T. H. P.

The Dithiocarbamate Accelerators of Vulcanisation. D. F. TWISS, S. A. BRAZIER, and F. THOMAS (J. Soc. Chem. Ind., 1922, 41, 83—88r).—The dithiocarbamate accelerators of vulcanisation

include the alkylthiocarbamates, the corresponding thiouram disulphides, and the xanthates. Unlike aldehyde-ammonia and the simple amines, the effectiveness of these compounds as vulcanisation catalysts is influenced to a remarkable extent by the presence of zinc oxide. Their use with zinc oxide gives rise to vulcanised products of exceptionally high tensile strength and resistance to extension, and accelerates the physical alteration of the rubber in a greater degree than the chemical alteration, as indicated by the combination of caoutchouc with sulphur. The alkylammonium alkylthiocarbamates and thiouram disulphides derived from secondary amines are much more powerful catalysts than the corresponding derivatives of primary amines. It is remarkable that in the absence of zinc oxide even the zinc dialkylthiocarbamates and zinc ethylxanthate are relatively feeble in their action, and that with the last-named substance a high vulcanisation temperature is unfavourable. When applied in the presence of a limited proportion of zinc oxide, thiocarbanilide causes the development of a discontinuous progress of vulcanisation similar to that described earlier for thiocarbo-*p*-toluidide. (See also Twiss and Brazier, A., 1920, i, 751; Twiss and Howson, A., 1920, i, 751; Twiss, A., 1921, i, 876.) D. F. T.

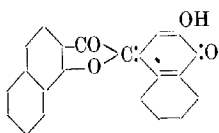
The Constitution of Catechin. IV. MAXIMILIAN NIERENSTEIN (T., 1922, 121, 604—613).

The Addition of Malonic Esters to Benzoylphenylacetylene. E. P. KOHLER (*J. Amer. Chem. Soc.*, 1922, 44, 379—385).—Malonic esters combine with benzoylphenylacetylene in the presence of sodium ethoxide to give compounds of the type $\text{C(Ph)CH(CPh)CH(CO}_2\text{Me)}_2$, which, however, immediately lose alcohol and pass into α -pyrone derivatives, having the ester group in the position 3. These pyrone derivatives are characterised by the fact that on treatment with alkalis they can be hydrolysed without breaking the pyrone ring, the product being either the pyrone acid or the corresponding pyrone. In this way, the author has prepared 2:4-diphenyl-6-pyrone-5-carboxylic acid, in the form of its methyl ester, m. p. 129°, its ethyl ester, m. p. 119°, and its sodium salt. The free acid when heated for two hours at 210—212° gives 2:4-diphenyl-6-pyrone, m. p. 142°, which by solution in alcoholic potassium hydroxide and subsequent addition of acid gives γ -benzoyl- β -phenylcrotonic acid, m. p. 130°, giving a methyl ester, m. p. 36°. A second acid, apparently isomeric with the crotonic acid, was also obtained during this opening of the pyrone ring, but it could not be isolated in the pure state.

The pyrone esters when heated with aqueous ammonia give ammonium salts of amino-compounds, but with concentrated alcoholic ammonia at the ordinary temperature they are slowly converted into a mixture of hydroxypyridine esters and the corresponding hydroxypyridines. Of these 6-hydroxy-2:4-diphenylpyridine, m. p. 210°, and ethyl 6-hydroxy-2:4-diphenylpyridine-5-carboxylate, m. p. 197°, have been prepared. W. G.

The Oxidation of α -Dinaphthaxanthens. HEMENDRA KUMAR SEN-GUPTA and STANLEY HORWOOD TUCKER (T., 1922, 121, 557—568).

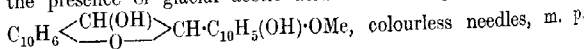
Autoxidation of 2-Acetyl- α -naphthol in Alkaline Solution. K. FRIES and H. LEUE (Ber., 1922, 55, [B], 753—763).—Solutions of 2-acetyl- α -naphthol in sodium or potassium hydroxide which contain more than one molecular proportion of the hydroxide to one of the acetyl derivative are completely stable towards air, even when heated; on the other hand, when an excess of base is avoided, the acetyl compound is readily oxidised to acetic acid



and a substance, $C_{22}H_{12}O_4$, to which, on account of its synthesis and reactions, the annexed constitution is assigned. The course of the reaction has not yet been elucidated fully, and it has not been found possible to isolate any intermediate product. The completely inhibitive effect of even a slight excess of alkali hydroxide is attributed to the existence of two types of salts of 2-acetyl- α -naphthol, of which only that which predominates in solutions of smaller hydroxyl-ion concentration is autoxidisable.

If oxygen is passed through a boiling solution of 2-acetyl- α -naphthol in alcohol which has been treated with an amount of sodium hydroxide solution insufficient for complete combination, ethyl acetate is produced and a dense precipitate of the sodium salt, $C_{22}H_{11}O_4Na$, black crystals, separates. The parent compound, $C_{22}H_{12}O_4$ (see above), crystallises in dark red needles, m. p. 306°; the *acetate*, lustrous, orange-yellow needles, m. p. 284°, *carbethoxy-derivative*, orange-coloured, silky needles, m. p. 239°, and *methyl ether*, slender red needles, m. p. 264°, are described. The compound, $C_{22}H_{12}O_4$, is reduced by a saturated solution of stannous chloride in glacial acetic acid to the corresponding trihydroxy-*derivative*, $C_{10}H_6<\begin{smallmatrix} CH(OH) \\ O \end{smallmatrix}>CH-C_{10}H_5(OH)_2$, yellow leaf-

lets, m. p. 195°, which is oxidised slowly to the parent substance on exposure to air, rapidly in alkaline solution. It gives a *triacetate*, colourless leaflets, m. p. 212°. The methyl ether, m. p. 264°, undergoes a peculiar transformation under the influence of alkali hydroxide, being converted by loss and subsequent addition of a molecule of water into the *diketone*, $OH-C_{10}H_6-CO-CO-C_{10}H_5(OH)OMe$, yellow needles, m. p. 186°, which is reconverted into the red methyl ether when heated above its melting point or treated with concentrated acid; it gives a well-defined *calcium salt*, $C_{22}H_{14}O_5Ca$, small, pale yellow needles, and is converted by *o*-phenylenediamine into the *quinoxaline derivative*, small, red, prismatic crystals, m. p. above 300° (decomp.) after softening at 270°. The diketone and also the red methyl ether are reduced by stannous chloride in the presence of glacial acetic acid to the *dihydroxy-compound*,



198° (*diacetate*, m. p. 185°), which is oxidised by ferric chloride to the red methyl ether.

The compound $C_{22}H_{12}O_4$ is converted by short ebullition with aniline into anilino- β -naphthaquinone, m. p. 245°. This observation has provided the key to the synthesis of the compound which is obtained by boiling a saturated solution of 6 : 7-benzocoumaranone and anilino- β -naphthaquinone (which behaves as 2-hydroxy-1 : 4-naphthaquinone-4-anil) in glacial acetic acid. H. W.

Strychnos Alkaloids. XXXI. Violet and Green Colour Reactions of Cacothelin. HERMANN LEUCHS [and, in part, KACHRN] (*Ber.*, 1922, 55, [B], 724—732).—The recognition of cacothelin as a quinone, $C_{21}H_{21}O_7N_3.HNO_3$ (this vol., i, 362), has necessitated a re-examination of its colour reactions. It is found that the violet salts are derived from the corresponding quinol. The unusual deepening of the colour, however, can only be explained by the assumption that fresh quinoid linkings are developed to replace those lost during the conversion of quinone into quinol. Information on this point is derived from a study of the esterification of the "nitroquinol" which, under regulated conditions, gives violet salts of a mono-ester and ultimately similar salts of di-esters. Since the formula of the nitroquinol in so far as it has been elucidated, $C_{16}H_{17}.C(OH) \dots C(OH); :C(NO_2); :N; :NH; \cdot CO_2H; :CH(OH)$, only indicates the possibility of the production of a mono-ester, the formation of a di-ester can only be explained by the hypothesis that the nitro- passes into the *isonitro*-group, $:C \begin{smallmatrix} \diagup N \\ \diagdown O \end{smallmatrix} \rightarrow :C \begin{smallmatrix} \diagup N \\ \diagdown OH \end{smallmatrix}$. This rearrangement involves the production of a new quinoid arrangement. Evidence obtained during the acetylation of the "nitroquinol" points to the conclusion that the migrating hydrogen atom is supplied by the imino-group.

The free "nitroquinol" is obtained by the addition of alkali hydroxide to a solution of the violet hydrochloride in boiling water and in an atmosphere of hydrogen. The violet salts are obtained readily from it by use of the requisite acid if precautions are taken to exclude air; the sulphate, hydrochloride, nitrate, and *hydrobromide* have been examined. Methyl sulphate converts the base into the compound, $C_{23}H_{23}O_{11}N_3S$, dark violet prisms.

The hydrochloride of the nitroquinol is converted by methyl alcohol and hydrogen chloride in the presence of acetone into the *hydrochloride* of the corresponding methyl ester, long, almost black needles, and by more drastic treatment in the absence of acetone into methylnitroquinol *methyl* ester, hydrochloride, lemon-yellow plates, $C_{23}H_{27}O_7N_3.HCl.2HCl.3MeOH$, or violet prisms, $C_{23}H_{27}O_7N_3.HCl.3H_2O$. With ethyl alcohol, the compounds $C_{23}H_{27}O_7N_3.HCl$, reddish-violet, quadratic leaflets and $C_{25}H_{31}O_7N_3.HCl$, tile-red, slender needles, are produced.

The "nitroquinol" hydrochloride is converted by acetic anhydride at 100° in the absence of air into the "*diacetyl nitroquinol*" *anhydride*, dark yellow prisms, from which the corresponding *monoacetate*,

$C_{23}H_{23}O_7N_3$, red crystals which become discoloured at 230° , is derived; the *sulphate*, *hydrochloride*, and *hydrobromide* were prepared.
H. W.

Preparation of Neutral Soluble Double Compounds of the Alkyl Xanthines and their N-Acyl Derivatives. KNOLL & Co. (D.R.-P. 340744; from *Chem. Zentr.*, 1921, iv, 1102—1103).—Dialkyl xanthines and their N-acyl derivatives form soluble crystalline salts with alkali benzoates and salicylates. The following double compounds are mentioned: theophylline-sodium salicylate; theobromine-sodium salicylate; N-acetyltheobromine-sodium salicylate; theophylline-sodium benzoate; N-acetyltheobromine-lithium salicylate; N-acetyltheobromine-ammonium salicylate; N-acetyl theobromine-potassium salicylate; theophylline-sodium salicylate; theophylline-potassium benzoate. G. W. R.

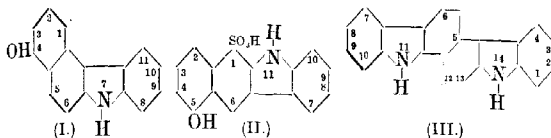
1-Phenyl-4-pyridone. ALEXANDER P. SMIRNOV (*Ber.*, 1922, 55, [B], 612—613; cf. A., 1921, i, 594).—In reply to Borsche and Bonaeker (this vol., i, 50), the author considers that the evidence brought forward favours his view of the internal ammonium oxide structure of the compound and not the ketonic constitution.

Anhydrous 1-phenyl-4-pyridone has m. p. 126° when slowly heated instead of 116° as recorded by Borsche and Bonaeker (*loc. cit.*).
H. W.

Synthesis of Quinic Acid. ADOLF KAUFMANN (*Ber.*, 1922, 55, [B], 614—616).—In his recent communication (this vol., i, 172, 174) on the synthetic production of quinic acid in quantity, Halberkann appears to have overlooked the work of Kaufmann and his colleagues (cf. A., 1909, i, 958; 1911, i, 749, 750; 1912, i, 651; 1918, i, 187).
H. W.

The Action of Sulphites on Aromatic Amino- and Hydroxy-compounds. IX. 6-Amino- α -naphthol-5-sulphonic Acid (A-Acid) and the Sulphite Reaction. HANS TH. BUCHERER and RUDOLF WAHL (*J. pr. chem.*, 1921, [ii], 103, 253—276).—A-Acid, when boiled with 40% sodium hydrogen sulphite, is converted into the *disulphurous acid* ester of 1:6-dihydroxynaphthalene-5-sulphonic acid, the sodium salt of which, $C_{10}H_6S_3O_6Na_2$, separates in long, colourless needles. The dihydroxynaphthalenesulphonic acid itself could not be isolated, being exceedingly soluble. A-Acid, with 40% ammonium sulphite and ammonia, yields 2:5-diaminonaphthalene-1-sulphonic acid, prismatic crystals and rectangular prisms, whilst with aniline and sodium hydrogen sulphite it yields 6-anilino- α -naphthol, which was isolated as the *monobenzoyl* derivative, m. p. 128.5° . With phenylhydrazine and sodium hydrogen sulphite, the corresponding phenylhydrazino-compound, apparently to be postulated as an intermediate stage, undergoes a further series of reactions (cf. following abstract), and the final products are 4-hydroxypheno- β -naphthacarbazole, I, m. p. 215° , 5-hydroxypheno- $\beta\beta$ -naphthacarbazole-1-sulphonic acid, II,

and *diphenonaphthadiazole*, III (?), m. p. 209°, I and III involving the elimination of a sulphonic acid group.

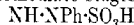



In the same way, phenylhydrazine and sodium hydrogen sulphite acts on 6-amino- α -naphthol-3:5-disulphonic acid to give, not only 5-hydroxypheno- β -naphthacarbazole-1:3-disulphonic acid, but also small quantities of 4-hydroxypheno- β -naphthacarbazole-2-sulphonic acid.

Sodium hydrogen sulphite, either alone or with aniline, appears to have no action on β -naphthylamine-1:5-disulphonic acid.

W. O. K.

The Action of Sulphites on Aromatic Amino- and Hydroxy-compounds. X. Action of Phenylhydrazine-Bisulphite Mixture, Particularly on Aminonaphtholsulphonic Acids, and Azo-dyes. HANS TH. BUCHERER and WALTHER ZIMMERMANN (*J. pr. Chem.*, 1921, [ii], 103, 277—315).—Bucherer and various co-workers have shown (cf. A., 1908, i, 455; A., 1909, i, 521; A., 1910, i, 144) that the action of a mixture of phenylhydrazine and 40% sodium hydrogen sulphite on certain naphtholsulphonic acids leads to the formation of phenonaphthacarbazole derivatives, and other naphtholsulphonic acids have now been investigated. Carbazole formation takes place in the case of β -naphthol-8-sulphonic acid, α -naphthylamine-7-sulphonic acid, 7-amino- α -naphthol-3-sulphonic acid (γ -acid), 6-amino- α -naphthol-3-sulphonic acid (J -acid), 5-amino- α -naphthol-3-sulphonic acid (M -acid). Usually the N -sulphonic acid of the carbazole is first formed, and this loses its N -sulphonic group on acid hydrolysis. The following compounds have been analysed: sodium pheno- β -naphthacarbazole-1:7-disulphonate, white needles; sodium pheno- α -naphthacarbazole-2-sulphonate; sodium 4-hydroxypheno- α -naphthacarbazole-2-sulphonate, opalescent leaves. Sodium pheno- β -naphthacarbazole-1:7-disulphonate when boiled with acid loses both sulphonic acid groups, giving pheno- α -naphthacarbazole, m. p. 132° (acetyl derivative, m. p. 149°). In the cases of 5-amino- α -naphthol-3-sulphonic acid and of α -naphthylamine-7-sulphonic acid, the corresponding diaryl hydrazine- N -sulphonic acids (which are presumably intermediate stages



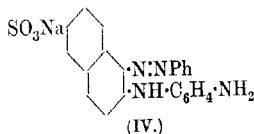
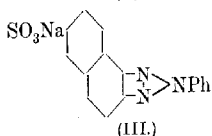
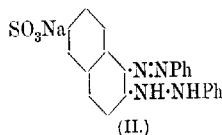
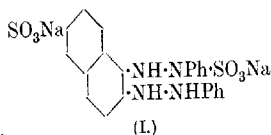
in the carbazole formation) of the type SO_3Na 

are also formed, whilst in the cases of 8-amino- α -naphthol-5-sulphonic acid (S -acid) and 8-amino- α -naphthol-3:5-disulphonic

acid (*K*-acid) no carbazole formation could be detected. From these diarylhydrazine-*N*-sulphonic acids from *S*-acid, and from α -naphthylamine-7-sulphonic acid, *azo*-compounds are formed by the action of alkali hydroxide of the formulæ $C_{16}H_{11}ON_2 \cdot SO_3Na$ and $C_{16}H_{11}N_2SO_3Na$ respectively.

K-Acid and *M*-acid, when boiled with sodium hydrogen sulphite, yield "dioxy-*K*-acid," and "dioxy-*M*-acid" as greyish-white precipitates; that is, the amino-groups are replaced by hydroxyl. These give with diazotised *p*-toluidine red dyes. "Dioxy-*K*-acid" (1:8-dihydroxynaphthalene-3:5-[4:6]disulphonic acid), on long boiling with concentrated hydrochloric acid, loses a sulphonic acid group to give 1:8-dihydroxynaphthalene-3-(6)-sulphonic acid.


The action of phenylhydrazine and sodium hydrogen sulphite on *azo*-dyes has been reinvestigated (cf. Bucherer and Sonnenberg, A., 1910, i, 144). The yellow product obtained from croceine (1-benzeneazo- β -naphthol-6-sulphonic acid) has apparently the constitution I, and with alkali hydroxide forms the red dye, II, which crystallises in long needles; its constitution is verified by the following reactions. With nitrite it loses aniline, and forms the triazole, III, and on reduction it forms 1:2-naphthylene-diamine-6-sulphonic acid, the properties agreeing with those of this compound as described by Witt (A., 1889, i, 270). The red compound, II, with concentrated hydrochloric acid undergoes a semidine transformation to give 1-benzeneazo-2-*p*-aminophenyl-amino-6-sulphonic acid, IV, the sodium salt of which crystallises in long, fine needles.



Similar yellow and red compounds are obtained from 1-*p*-acetylaminobenzenazo- β -naphthylamine-6-sulphonic acid, whilst the action of phenylhydrazine and sodium hydrogen sulphite on naphthol-blue-black (8-amino-2-benzeneazo-7-*p*-nitrobenzeneazo- α -naphthol-3:6-disulphonic acid) is due simply to the sodium hydrogen sulphite, and the dye is reduced to 7:8-diamino-2-benzeneazo- α -naphthol-3:6-disulphonic acid, a bluish-red dye. This gives a brownish-red dye with phenanthraquinone, which separates in small needles, and is turned yellow by mineral acids. W. O. K.

Derivatives of Benzthiazole. E. ROMANI (*Gazzetta*, 1922, 52, i, 29—32).—Thiolbenzthiazole, first prepared by Hofmann

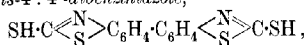
(A., 1887, 823, 1039; cf. Jacobson and Frankenbacher, A., 1891, i, 1048), may be obtained easily and cheaply by heating with sulphur at 260° in a closed space either phenylthiocarbamide or thiocarbanilide or methyleneaniline, phenylthiocarbimide being formed as an intermediate product; the yield of the pure compound amounts to 75–80%. 1-Thiolbenzthiazole is a moderately energetic acid and forms salts of the formula $[C_6H_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} CS]_2X$.

1-Thiol-5-methylbenzthiazole, , prepared from *p*:*p*-ditolylthiocarbamide and sulphur, forms white crystals, m. p. 177°.

1-Thiol-6-(or 4)-methylbenzthiazole, similarly obtained, has m. p. 161°.

1-Thiol-3-methylbenzthiazole, has m. p. 185°.

1:1'-Dithiolbis-4:4'-dibenzthiazole,



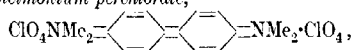
prepared from *p*:*p*-diphenylenethiocarbamide, forms dark yellow crystals, m. p. 320°, and in alkaline solution readily forms salts of the heavy metals.

T. H. P.

The Blue Oxidation Product of Diphenylamine. F. KEHRMANN and G. ROY (*Ber.*, 1922, 55, 156–158).—It was shown by Kehrmann and Micewitz (A., 1912, i, 1020) that the blue product formed by oxidation of diphenylamine with nitric acid in concentrated sulphuric acid is an imonium salt of *N*:*N'*-diphenylbenzidine. In view of doubts thrown on this explanation (this vol., i, 28), further experiments have been made. By oxidation in 60% sulphuric acid with potassium nitrate, the quinhydrone salt of *N*:*N'*-diphenylbenzidine was isolated and was reduced to diphenylbenzidine, m. p. 234–235°. When oxidising in concentrated sulphuric acid, it is necessary to remove nitrous acid by means of a current of air, since this reacts with the imonium salt on diluting, forming products which cannot be reduced to diphenylbenzidine. By oxidation with manganese dioxide in 80% sulphuric acid, a yield of 62% of the theory was obtained.

E. H. R.

The So-called Peroxidation Products of Leuco-triphenylmethane Dyes. F. KEHRMANN, GUSTAVE ROY, and MARIE RAMM (*Helv. Chim. Acta*, 1922, 5, 153–157).—It is well known that if excess of lead peroxide be used for the preparation of triphenylmethane dyes from their leuco-compounds, the yield and quality of the product are unsatisfactory. It is now shown that by gradual treatment at the ordinary temperature of a malachite-green solution, not too dilute and acidified with sulphuric acid, with lead peroxide until a diluted sample shows no green tinge, and addition of the filtered solution to perchloric acid, tetramethyl-diphenylquinoneimonium perchlorate,



is precipitated in the form of orange needles, benzoic acid being present in solution. The same perchlorate results from the oxidation of tetramethylbenzidine. Similarly, brilliant-green and tetraethylbenzidine furnish *tetraethyldiphenoquinoneimonium perchlorate*, $C_{20}H_{28}O_8N_2Cl_2$. The same products, with carbon dioxide, were obtained from Michler's hydrol and the corresponding tetraethyl derivative (cf. Rosenstiehl, A., 1895, i, 541). Further, the formation of dinitrotetramethylbenzidine by treatment of tetramethylbenzidine with dilute nitric acid (Bourgeois, *Bull. Soc. Ind. Rouen*, 1882, 503) or nitrous acid (Michler and Pattinson, A., 1882, 199) is preceded by that of tetramethyldiphenoquinoneimonium salts, of which quantitative yields may be obtained in the latter case.

J. K.

Preparation of New Therapeutically Active Acridine Derivatives. FAIRWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 176038).—Therapeutically active acridine derivatives having a bactericidal action are obtained by introducing into the 9-position of acridine, or of its substitution products, an amino-, or substituted amino-group, the substituents being any organic radicles other than aryl groups. These compounds are obtained by causing ammonia or a primary or secondary amine (other than an arylamine) to act on a 9-halogen acridine or a 9-alkoxy- or phenoxy-acridine in presence or absence of a catalyst such as a copper salt. They may also be obtained by reducing a 9-hydrazino-acridine or a 9-nitroacridine, or by decomposing the azides of 9-acridine-carboxylic acids with elimination of nitrogen, or finally by the action of a hypochlorite or hypobromite on the amide of a 9-acridinecarboxylic acid. The following briefly summarises the detailed examples given in the patent specification for the preparation of these acridine derivatives by these various methods, and of the necessary intermediate products. *2-Ethoxy-9-ethanolamino-acridine*, yellow crystals, m. p. 146° , is obtained by mixing aminoethanol with 2-ethoxy-9-chloroacridine in alcoholic solution at 100° . *2-Ethoxy-9-p-hydroxyphenylethylaminoacridine*, m. p. 233° , is similarly obtained from *p*-hydroxyphenylethylamine. *2-Ethoxy-9-antipyrineaminoacridine*, a yellowish-red base, m. p. 257° , is prepared similarly from 4-aminoantipyrine. *9-Aminoacridine* forms yellow needles, m. p. 236° , and gives a water-soluble *hydrochloride*. It may be obtained by heating 9-chloroacridine with alcoholic ammonia at 140° in presence of copper acetate, or alternatively by heating alcoholic ammonia with 9-ethoxyacridine at 120° for several hours. The reduction of 9-phenylhydrazinoacridine hydrochloride with zinc dust and acetic acid or other reducing agents also furnishes 9-aminoacridine, as also does the decomposition of the amide of acridine-9-carboxylic acid by digestion in a ball mill with potassium hypobromite. The *9-chloroacridine* and its derivatives required for the above preparations are obtained from the corresponding acridones or directly from the arylanthranilic acids by heating them with phosphorus penta- or oxy-chloride. *9-Ethoxyacridine* is obtained by the action of sodium ethoxide on 9-chloro-

acridine; it melts at 83° , and yields acridone when heated with a mineral acid. 2:9-Diethoxyacridine forms fine needles, m. p. 83° . The hydrazinoacridine derivatives are produced by treating 9-halogenacridines with hydrazines. 9-Phenylhydrazinoacridine forms yellow needles, m. p. $173-174^{\circ}$; 2-ethoxy-9-phenylhydrazinoacridine is a light yellow powder, m. p. $232-234^{\circ}$; 9-hydrazinoacridine, $C_{13}H_8N \cdot NH \cdot NH_2$, forms orange needles from alcohol, m. p. 169° ; hydrazino-9:9-bisacridine, $C_{13}H_8N \cdot NH \cdot NH \cdot C_{13}H_8N$, forms dark red crystals, m. p. 265° . 9-Diethylamino-2-ethoxyacridine is prepared by heating 9-chloro-2-ethoxyacridine with diethylamine in alcoholic solution at $130-140^{\circ}$ for six hours in presence of cuprous chloride and copper bronze. The base itself is a thick oil, and it gives a red, crystalline hydrochloride, m. p. 177° . 9-Piperidino-2-ethoxyacridine is prepared in a similar way, using piperidine instead of diethylamine. The base melts at 122° , and gives a water-soluble hydrochloride, m. p. 252° (with decomp.). 9-Ethylaminoacridine from 9-ethoxyacridine and alcoholic ethylamine is an oil which soon solidifies, and recrystallised from dilute alcohol has m. p. 129° . The nitration of 9-aminoacridine in concentrated sulphuric acid yields a dinitro-9-aminoacridine, a dark red base, m. p. above 300° , which on reduction with stannous chloride gives a triaminoacridine hydrochloride, long, yellow needles, and the free base, dark red laminae. 3:9-Diaminoacridine is prepared from 2-chloro-4-nitrobenzoic acid and aniline by way of 5-nitrodiphenylamine-2-carboxylic acid, 3-nitroacridine by elimination of water, 9-chloro-3-nitroacridine by the action of phosphorus pentachloride, yellow needles, m. p. 213° , and 3-nitro-9-aminoacridine, m. p. above 300° (with decomp.), and reduction of this with stannous chloride, or ferrous sulphate and ammonia. 3:9-Diamino-7-ethoxyacridine is prepared by a similar series of reactions starting with *p*-phenetidine instead of aniline. Of the intermediate substances, 4-nitro-2-*p*-phenetidino benzoic acid melts at $233-234^{\circ}$, 9-chloro-3-nitro-7-ethoxyacridine melts at $186-187^{\circ}$, 3-nitro-9-amino-7-ethoxyacridine is obtainable in two forms, red and yellow; crystallised from nitrobenzene it melts at 310° , and on reduction gives the diamino-ethoxyacridine, m. p. $123-124^{\circ}$ (with decomp.). The azide of acridine-9-carboxylic acid, $C_{13}H_8N \cdot CO \cdot N_3$, a very unstable substance decomposing even at the ordinary temperature, is obtained by the action of sodium nitrite on the hydrazine, m. p. 244° , prepared by heating the ester with hydrazine in alcoholic solution. On heating the azide in aqueous suspension, 9-aminoacridine is formed with evolution of nitrogen, whilst if the same decomposition is carried out in alcoholic solution, the urethane, $C_{13}H_8N \cdot NH \cdot CO_2Et$, crystallises on cooling. It melts at $188-194^{\circ}$ and on hydrolysis with 2*N*-sulphuric acid is converted into 9-aminoacridine sulphate. In a similar way, 2-chloro-9-aminoacridine, m. p. $272-274^{\circ}$, is obtained from 2-chloroacridine-9-carboxylic acid, m. p. 264° . The latter substance is synthesised from *o*-chlorobenzaldehyde and magnesium methyl iodide, which give *o*-chlorophenylethyl alcohol and by oxidation *o*-chloroacetophenone, b. p. $98^{\circ}/6$ mm. This is condensed with *p*-chloroaniline to 2-chloro-9-methylacridine, which by Kaufmann's

process (A., 1912, i, 655) is transformed into 2-chloro-9-aldehyde-acridine, m. p. 171—172°, which on oxidation gives the acid. Its ethyl ester melts at 71—72°, and the hydrazide at 210—211°. From this the azide is obtained by the action of nitrous acid, and on heating it in alcoholic solution the urethane, $C_{13}H_7NCl \cdot NH \cdot CO_2Et$, m. p. 205°, is formed. The latter on hydrolysis yields 2-chloro-9-aminoacridine. G. F. M.

Dissociation of the so-called 1:1'-Dibenzyltetrahydro-4:4'-dipyridyl. ERNST WEITZ (*Ber.*, 1922, 55, [B], 599—600; cf. Weitz and Ludwig, this vol., i, 365).—A reply to Emmert (A., 1909, i, 602; 1917, i, 221; 1919, i, 455; 1920, i, 331; this vol., i, 179). The di-iodide results from the bimolecular radicle formed with the aid of oxygen; the monoiodide is derived from the colourless product. H. W.

The Acylated and Alkylated Leuco-indigotins. E. GRANDMOUGIN (*Compt. rend.*, 1922, 174, 758—760).—The author is of the opinion that the acylation or alkylation of leuco-indigotin gives oxygen-substituted derivatives. The acylated derivatives on oxidation give nitrogen acylated derivatives of indigotin owing to the migration of the acyl group. The alkylated derivatives simply undergo saponification and regenerate indigotin. In support of this, it is shown that if methyl sulphate acts on an alkaline solution of indigo white, kept alkaline throughout, a new dimethyl derivative, m. p. 252° (decomp.), of leuco-indigotin is obtained, which on oxidation with nitrous acid regenerates indigotin, and on oxidation with chromic acid gives isatin. Acylation under similar conditions must also give an oxygen-substituted derivative, during the oxidation of which the acyl group migrates and the stable ketonic form of the indigotin results. W. G.

Electrochemical Studies in the Pyrazole Group. FR. FICHTER and HUGUES DE MONTMOLIN (*Helv. Chim. Acta*, 1922, 5, 256—262).—Electrochemical oxidation of a number of pyrazole derivatives results for the most part in the formation of carbon dioxide, with a small amount of subsidiary products. Thus from 1-phenyl-3-methylpyrazolone, a compound, $C_{21}H_{20}O_2N_4 \cdot 1\frac{1}{2}H_2O$, apparently methylenebisphenylmethylpyrazolone (Pellizzari, A., 1890, 646) is obtained. Oxidation apparently attacks the 4-position first, since 4-keto-1-phenyl-3-methylpyrazolone and antipyrine are completely destroyed with great rapidity. 1-Phenyl-3:4-dimethylpyrazolone is more resistant, and a small amount of bis-1-phenyl-3:4-dimethylpyrazolone is formed, identical with that prepared by oxidation with nitrous acid, or, better, dilute chromic acid solution. It is accompanied by a compound, $C_{18}H_{14}O_4N_2$, m. p. 242—243°, which is hydrolysed by warm concentrated sulphuric acid to bis-1-phenyl-3:4-dimethylpyrazolone (from oxidation of the phenyldimethylpyrazolone first produced) and fumaric acid, and is therefore probably 1-phenyl-3:4-dimethylpyrazolonyl-2-fumaric acid. Oxidation of 1-phenyl-3-methylpyrazole in acid suspension yields quinone, quinol, and oxalic acid, but no methyl-

pyrazole. From a suspension in potassium carbonate solution, however, pyrazole-3-carboxylic acid is produced. From 3:5-dimethylpyrazole, with sodium sulphate solution as electrolyte, a very small amount of pyrazole-3-carboxylic acid is formed. In these cases, therefore, the action of anodic oxygen is much more vigorous than that of alkaline permanganate (Claisen and Roosen, A., 1894, i, 346; Marchetti, A., 1893, i, 179; Rothenburg, A., 1894, i, 384), and it is noteworthy that oxidation of 1-phenyl-3-methylpyrazole by acid permanganate also destroys, not the pyrazole ring as in the above electrochemical oxidation, but the benzene nucleus (Knorr and Macdonald, A., 1894, i, 543). The electrochemical reduction of the bisulphite compound of 4-keto-1-phenyl-3-methylpyrazolone to 4-hydroxy-1-phenyl-3-methylpyrazolone (Knorr and Pschorr, D.R.-P. 75378) in satisfactory yield is described, as also is the formation of rubazonic acid by electrochemical reduction of 4-oximino-1-phenyl-3-methylpyrazolone, followed by anodic oxidation of the resulting 4-amino-1-phenyl-3-methylpyrazolone. J. K.

The Action of Diazomethane on Uracil. TREAT B. JOHNSON, ARTHUR J. HILL, and FRANCIS H. CASE (*Proc. Nat. Acad. Sci.*, 1922, 8, 44—45).—Diazomethane and uracil slowly react in dry ether to give 1:3-dimethyluracil. The reaction is applicable to pyrimidines of this type, and there is some indication that this reaction may furnish a method for the detection of replaceable hydrogens in the more complicated pyrimidine and purine glucosides. W. G.

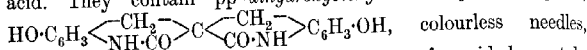
The Hydrolysis of Antipyrine Salicylate. I. M. KOLTHOFF (*Rec. trav. chim.*, 1922, 41, 135—144).—Antipyrine salicylate should be regarded as a salt of antipyrine and salicylic acid; it is much hydrolysed in aqueous solution. Its molecular solubility at 18° is 1.32×10^{-2} , its ionic product 6.2×10^{-6} , and its solubility product 1.2×10^{-4} . According to theory, its solubility in solutions of antipyrine should be less, whilst salicylic acid should have only a slight influence; experiment confirms these predictions.

H. J. E.

Spiran. IX. Preparation of Bishydrocarbohostyryl-3:3-spiran and its By-products. HERMANN LEUCHS and HANS VON KATINSZKY [with EVA CONRAD] (*Ber.*, 1922, 55, [B], 710—723).—The reduction of ethyl di-*o*-nitrobenzylmalonate to bishydrocarbohostyryl-3:3-spiran, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \cdot \text{CO} \end{smallmatrix} > \text{C} < \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \cdot \text{NH} \end{smallmatrix} > \text{C}_6\text{H}_4$, has been described by Lellmann and Schleich (A., 1887, 490) and by Radulescu (A., 1911, i, 498); the analytical data quoted by these chemists are not entirely satisfactory, and re-examination of their product has disclosed the presence of a number of chlorinated and oxygenated impurities, some of which have been identified. Suitable modification of their method of preparation leads to the isolation of the pure spiran, which is also obtained by a different process.

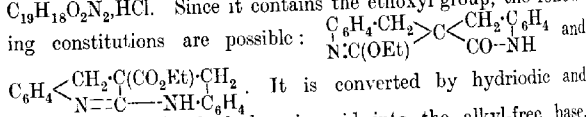
According to Radulescu (*loc. cit.*), ethyl di-*o*-nitrobenzylmalonate

is reduced by the gradual addition of concentrated hydrochloric acid to a solution of the ester in hot alcohol in the presence of granulated zinc. The crude spiran which is thereby precipitated is purified by solution in alcoholic potassium hydroxide, filtration, and precipitation with hydrochloric acid; as thus obtained, it is free from zinc, but contains chloro-derivatives which cannot be removed and gives a violet coloration with ferric chloride. It is more conveniently purified by glacial acetic acid, but a homogeneous product cannot thus be obtained. The filtrate from the spiran yields, when concentrated, a mixture of phenolic and neutral substances from which the former are isolated by protracted digestion with concentrated ammonia and subsequent precipitation with acid. They contain *pp'*-*dihydroxybishydrocarbostyryl-3:3-spiran*,



m. p. 265—268° (decomp.) (acetate, coarse, four-sided crystals, m. p. 177—179°), and *p-hydroxybishydrocarbostyryl-3:3-spiran*, thin, colourless needles or prisms, decomp. 255—285° [acetate, needles, m. p. 246—248° (decomp.)]. The final residues from the preparation of the spiran contain a basic substance, $\text{C}_{19}\text{H}_{18}\text{O}_2\text{N}_2$, long, colourless needles, m. p. 192—194° (see later).

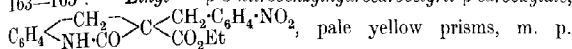
Bishydrocarbostyryl-3:3-spiran is prepared in 65—80% yield by dissolving ethyl di-*o*-nitrobenzylmalonate in semi-saturated alcoholic hydrogen chloride solution at -5° to +10° and gradually adding zinc dust; when hydrogen has been evolved freely for some time, the solution is filtered, the filtrate is diluted with an equal volume of water and heated on the water-bath, whereon the spiran separates. It crystallises in broad, lustrous needles, m. p. 350—360°, after darkening at 320°, and sublimes almost without decomposition at 300°/15 mm. The basic substance, $\text{C}_{19}\text{H}_{18}\text{O}_2\text{N}_2$ (cf. above), is isolable from the filtrates from the spiran and its nature is established by the isolation of a well-defined *hydrochloride*, $\text{C}_{19}\text{H}_{18}\text{O}_2\text{N}_2\cdot\text{HCl}$. Since it contains the ethoxyl group, the following constitutions are possible:



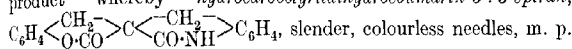
It is converted by hydriodic and acetic acids or by hydrobromic acid into the alkyl-free base, $\text{C}_{16}\text{H}_{14}\text{N}_2$, m. p. 217—218°, which has been described by Reissert as Δ -*N*-tetrahydronaphtholine, but the reaction is of little value in elucidating its constitution. Evidence in favour of the lactim ether formula is based on the observations that it does not yield an acetyl derivative with acetic anhydride, and that it can be prepared from the hydrocarbostyrylsiran by conversion into the imide chloride (cf. Radulescu, *loc. cit.*) and treatment of the latter with sodium ethoxide.

An improved method for the preparation of ethyl di- and mono-*o*-nitrobenzylmalonates is given, but only the former of these is crystalline; the reduction of the latter to ethyl hydrocarbostyryl- β -carboxylate is described. Similar results are recorded with the methyl esters; *methyl di-o-nitrobenzylmalonate* crystallises in colour-

less plates or coarse prisms, m. p. 137—138°, whereas *methyl mono-o-nitrobenzylmalonate* is a yellow liquid which is reduced to *methyl hydrocarbostyryl-β-carboxylate*, colourless, matted needles, m. p. 163—165°. *Ethyl β-o-nitrobenzylhydrocarbostyryl-β-carboxylate*,



pale yellow prisms, m. p. 143.5—144.5°, is prepared by the action of *o*-nitrobenzyl chloride and sodium ethoxide on ethyl hydrocarbostyryl-β-carboxylate, and is reduced to bishydrocarbostyryl-3:3-spiran. The conversion of the above ester or of ethyl di-*o*-nitrobenzylmalonate into the spiran takes place with the intermediate formation of the corresponding amino- or diamino-esters; these are too unstable to be isolated in substance, but their formation is demonstrated by diazotisation and subsequent boiling of the diluted solutions of the reduction product whereby *hydrocarbostyryldihydrocoumarin-3:3-spiran*,



slender, colourless needles, m. p. about 280° after previous softening, and *bishydrocoumarin-3:3-spiran*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{CO} \end{array} \text{C} \begin{array}{c} \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{O} \end{array} \text{C}_6\text{H}_4$, colourless plates, m. p. 237°, are obtained.

H. W.

A Method for Making Methyl-violet. HENRY JERMAIN MAUDE CREIGHTON (*Proc. Nova Scotia Inst. Sci.*, 1922, **15**, [i], 57—61).—A method is described by which, by the oxidation of dimethylaniline with copper sulphate in presence of phenol and sodium chloride, methyl-violet, a mixture of the hydrochlorides of penta- and hexa-methylpararosaniline, can be obtained in 75—85% yield. [*Cf. J. Soc. Chem. Ind.*, 1922, 323A.]

E. H. R.

Behaviour of Azides of Acids. E. OLIVERI-MANDALÀ (*Gazzetta*, 1922, **52**, i, 101—106).—The formation of azides of carbamic acids by the interaction of alkylcarbimides with azoimide (Schroeter, A., 1909, i, 617; Oliveri-Mandalà and Noto, A., 1913, i, 774; Oliveri-Mandalà and Calderaro, A., 1913, i, 961) is found to be a reversible reaction, $\text{R} \cdot \text{N} \cdot \text{CO} + \text{N}_3\text{H} \rightleftharpoons \text{NHR} \cdot \text{CO} \cdot \text{N}_3$, since addition of phenylcarbylamine to a hot benzene solution of the azide results in the formation of 1-phenyltetrazole, owing to the fixation of the liberated azoimide by the carbylamine. Unlike the azides of carbamic acids, those of thiocarbamic acids, when heated in an indifferent solvent or in aqueous hydrochloric acid, yield polymers of the corresponding alkyleyanamides (Freund and Hempel, A., 1895, i, 193; Freund and Schwarz, A., 1897, i, 125; Oliveri-Mandalà, A., 1914, i, 1144), derivatives of tetrazole thus being obtainable directly from thiocarbimides by means of the following reactions: (1) $\text{R} \cdot \text{N} \cdot \text{CS} + \text{N}_3\text{H} \rightarrow \text{NHR} \cdot \text{CS} \cdot \text{N}_3 \rightarrow$ (2) $\text{NHR} \cdot \text{C} \cdot \text{N}$, (3) $\text{NHR} \cdot \text{C} \cdot \text{N} + \text{N}_3\text{H} \rightarrow \text{NHR} \cdot \text{C}(\text{N}_3) \cdot \text{NH} \rightarrow$ (4) $\text{N} \begin{array}{c} \text{N} \cdot \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{C} \cdot \text{NHR} \end{array}$.

The reaction of azoimide on methylthiocarbimide yields a compound, $\text{C}_2\text{H}_5\text{N}_6$, which crystallises in small needles, m. p. 218°.

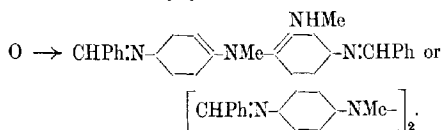
and is probably formed in accordance with the scheme $\text{NMe}\cdot\text{C}\cdot\text{NH} + \text{N}_3\text{H} = \text{NMe}\cdot\text{C}(\text{N}_3)\cdot\text{NH}_2 \rightarrow \text{N} \begin{smallmatrix} \nearrow \text{N}\cdot\text{NMe} \\ \searrow \text{N}\cdot\text{C}\cdot\text{NH}_2 \end{smallmatrix}$.

In view of the formation of azides by treatment of the sodium derivative of azoimide with acid chlorides (Schroeter, A., 1909, i, 773), an attempt has been made to prepare nitrosoazide, $\text{O}\cdot\text{N}\cdot\text{N}\cdot\text{N}\cdot\text{N}$ or $\text{O}\cdot\text{N}\cdot\text{N} \begin{smallmatrix} \nearrow \text{N} \\ \searrow \text{N} \end{smallmatrix}$ or $\text{O} \begin{smallmatrix} \nearrow \text{N}\cdot\text{N} \\ \searrow \text{N}\cdot\text{N} \end{smallmatrix}$, by the action of nitrosyl chloride on sodium azoimide in ethereal solution. The readiness with which the action takes place and the liberation of nitrous oxide and nitrogen in equal volumes indicate the initial addition of azoimide to nitrous acid, thus: $\text{O}\cdot\text{NH}\cdot\text{O} + \text{N}_3\text{H} = \text{O}\cdot\text{NH}(\text{N}_3)\cdot\text{OH}$, the unstable additive compound then decomposing into $\text{H}_2\text{O} + \text{N}_2 + \text{N}_2\text{O}$. A further proof of the instability of inorganic compounds containing the triazo-group is furnished by the results of several attempts to obtain the compound $\text{N}_3\cdot\text{OH}$ by decomposing iodoazide (Hantzsch, A., 1900, ii, 274) by means of water and potassium hydroxide at low temperatures.

T. H. P.

Basic Properties of the Hydrazones. II. R. CIUSA and L. VECCHIOTTI (*Gazzetta*, 1922, 52, i, 128—134; cf. A., 1921, i, 749).—In the formation of an additive compound of a phenylhydrazone with one molecule of each of two aromatic polynitro-derivatives, one and the same compound results, no matter in which order the two polynitro-derivatives are added.

In order to ascertain the influence of substitution of methyl for the methinic hydrogen of benzaldehyde phenylhydrazone on the coloration of the halochromic hydrochloride, the action of gaseous hydrogen chloride on benzaldehyde phenylmethylhydrazone in ethereal solution has been investigated. As with the phenylhydrazone, an orange-yellow hydrochloride is obtained, but on hydrolysis this yields, not the original phenylmethylhydrazone, but a compound, $\text{C}_{23}\text{H}_{26}\text{N}_4$, which corresponds with two mols. of the phenylmethylhydrazone less one mol. of hydrogen and yields benzaldehyde and a compound, $\text{C}_{14}\text{H}_{18}\text{N}_4$, when hydrolysed. The formation of the compound $\text{C}_{23}\text{H}_{26}\text{N}_4$ probably takes place according to the scheme: $2\text{C}_6\text{H}_5\cdot\text{NMe}\cdot\text{N}\cdot\text{CHPh} \rightarrow 2\text{CHPh}\cdot\text{N} \begin{smallmatrix} \diagup \text{NHMe} \\ \diagdown \end{smallmatrix}$

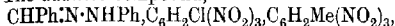


Under similar experimental conditions, anisaldehyde phenylmethylhydrazone yields a compound, $\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}_2$, which is isomeric with the phenylmethylhydrazide of anisic acid.

The additive compound,

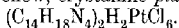
$\text{CHPh}\cdot\text{N}\cdot\text{NHPh}\cdot\text{C}_6\text{H}_4\text{Cl}(\text{NO}_2)_3\cdot\text{OH}\cdot\text{C}_6\text{H}_4(\text{NO}_2)_3$,
formed by benzaldehyde phenylhydrazone with picryl chloride and

picric acid, crystallises in lustrous, reddish-brown needles, m. p. 94–95°. The *additive* compound,



formed by the same hydrazone with picryl chloride and trinitrotoluene, forms reddish-brown needles, m. p. 82°.

The compound $\text{C}_{25}\text{H}_{28}\text{N}_4$ (*vide supra*) crystallises in small, white needles, m. p. 155°, and in acetic acid solution or when suspended in an acid medium rapidly turns successively green, blue, and violet. The compound $\text{C}_{14}\text{H}_{18}\text{N}_4$ rapidly reduces Fehling's solution and yields a greenish-yellow, crystalline *platinichloride*,



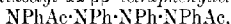
The compound $\text{C}_{15}\text{H}_{16}\text{O}_2\text{N}_2$ (*vide supra*) crystallises in colourless needles, m. p. 233°.

Benzophenonediphenylhydrazone, $\text{C}_{25}\text{H}_{20}\text{N}_2$, forms long, yellow needles, m. p. 145°, and, like tetraphenylhydrazine, yields coloured salts and xylene and formamidine solutions which become more highly coloured when heated, so that the base must be regarded as undergoing hydrolysis: $\text{CPh}_2\cdot\text{N}\cdot\text{NPh}_2 \rightleftharpoons \text{CPh}_2\cdot\text{N}^+ + \cdot\text{NPh}_2$.

T. H. P.

Amine-oxidation. III. Bivalent Nitrogen. Diarylacylhydrazyls. STEFAN GOLDSCHMIDT and KARL EULER (*Ber.*, 1922, 55, [B], 616–628).—The previous work on triphenylhydrazyl (A., 1920, i, 257) has been extended to α -acetyl(α -benzoyl)-diphenylhydrazyl and α -acetyl(α -benzoyl)-di-*p*-tolylhydrazyl. Evidence of dissociation rests partly on the failure of the solutions to obey Beer's Law, but mainly on the behaviour towards nitric oxide and triphenylmethyl. Results of determinations of molecular weight also indicate dissociation, but these are interpreted with considerable reserve on account of the instability of the solutions. The following order of dissociability is given: $\alpha\alpha'$ -diacetyltetraphenyltetrazen < $\alpha\alpha'$ -dibenzoyltetraphenyltetrazen < $\alpha\alpha'$ -diacetyl-tetra-*p*-tolyltetrazen < $\alpha\alpha'$ -dibenzoyltetra-*p*-tolyltetrazen.

A suspension of monoacetylhydrazobenzene in cold benzene is converted by lead peroxide in the presence of solid potassium carbonate into $\alpha\alpha'$ -diacetyl- $\alpha\alpha'$ - $\beta\beta'$ -tetraphenyltetrazen,



colourless, prismatic crystals, m. p. 126° (decomp.). The substance dissolves in chloroform to a very pale violet-brown solution; in cold toluene, it forms a pale yellow solution which becomes brownish-violet when heated, returning to yellow when cooled, but the operation cannot be repeated indefinitely on account of its instability. The tetrazone, when dissolved in benzene, is immediately decomposed by dry hydrogen chloride into acetanilide and *p*-chloroazobenzene. It combines with nitric oxide, but the product could not be caused to crystallise. (Acetylhydrazobenzene and nitrous fumes give *N*-nitroso-*N'*-acetylhydrazobenzene, a yellow, non-crystalline substance.)

$\alpha\alpha'$ -Dibenzoyl- $\alpha\alpha'$ - $\beta\beta'$ -tetraphenyltetrazen, m. p. 114° (decomp.), is prepared by the oxidation of *N*-benzoylhydrazobenzene, m. p. 138°; it gives pale green solutions in benzene, toluene, or chloroform

which undergo rapid decomposition at the atmospheric temperature. It combines readily with triphenylmethyl to give the compound $C_{38}H_{30}ON_2$, prismatic plates, m. p. $165-166^\circ$ (decomp.) after darkening at 120° . With nitric oxide, it yields the substance, $C_{19}H_{15}O_2N_3$, yellow, prismatic leaflets, m. p. 104° . The action of lead peroxide on *N*-benzoylhydrazobenzene, m. p. 126° (cf. Biehinger and Busch, A., 1903, i, 296; Freundler, A., 1903, i, 663) leads to the immediate formation of azobenzene.

N-Acetylhydrazo-*p*-toluene (from *p*-hydrazotoluene and acetic anhydride at $40-50^\circ$), almost colourless, prismatic platelets, m. p. 120° , is oxidised to $\alpha\alpha'$ -diacetyl- $\alpha\alpha'\beta\beta'$ -tetra-*p*-tolyltetrazen, colourless prisms, m. p. 109° (decomp.). It dissolves in chloroform to an initially colourless solution which rapidly becomes brownish-violet. With triphenylmethyl it gives the compound $C_{38}H_{32}ON_2$, colourless crystals, m. p. $156-157^\circ$ (decomp.).

Benzoyl-*p*-hydrazotoluene (cf. Biehinger and Busch, *loc. cit.*) is converted by lead peroxide into $\alpha\alpha'$ -dibenzoyl- $\alpha\alpha'\beta\beta'$ -tetra-*p*-tolyltetrazen, aggregates of needles, m. p. 115° (decomp.), which dissolves in organic media to solutions which are colourless initially, but very rapidly become green and are very unstable. It unites with triphenylmethyl to give the substance $C_{40}H_{34}ON_2$, colourless, prismatic crystals, m. p. $146-147^\circ$ (decomp.) after becoming discoloured at 144° .
H. W.

Preparation of *p*-Nitrophenylhydrazine and other Aromatic Hydrazines. WILLIAM DAVIES (T., 1922, 121, 715-721).

Amine-oxidation. IV. Bivalent Nitrogen. $\alpha\alpha$ -Diphenyl- β -trinitrophenylhydrazyl. STEFAN GOLDSCHMIDT and KONRAD RENN (*Ber.*, 1922, 55, [B], 628-643; cf. preceding page).—The elucidation of the exact relationship between triphenylhydrazyl and hexaphenyltetrazen (A., 1920, i, 257) is rendered difficult by the instability of these substances. The present communication is devoted to a description of attempts to prepare more stable hydrazyls, a suitable example being found in $\alpha\alpha$ -diphenyl- β -trinitrophenylhydrazyl, $NPh_2NC_6H_2(NO_2)_3$. . ., which exists entirely in the unimolecular form, and is so unusually stable that its molecular weight can be determined in solution with accuracy and certainty. The substance appears to be the nitrogen analogue of Schlenk's tri-triphenylmethyl (A., 1910, i, 236).

It is remarkable that the stability of the hydrazyls cannot be foretold from a consideration of the valency demand of the radicals and that they do not appear to conform to the regularities which have been established by Wieland for the dissociation of tetra-arylhydrazines. Signs of uniform behaviour can be detected within the group, but a general theory cannot be put forward until further members of the series have been prepared.

as-Diphenylhydrazine and *p*-benzoquinone give *benzoquinone-diphenylhydrazone*, $NPh_2N:C_6H_4O$, m. p. 136° , which is smoothly reduced by ammonium sulphide in alcoholic solution to the corresponding leuco-compound, $NPh_2NH:C_6H_4OH$; the latter is rather

unstable, particularly in the presence of alcohol or alkali hydroxide, and all attempts to methylate it were unsuccessful.

αα-Diphenylhydrazine reacts readily with picryl chloride in chloroform solution with almost quantitative production of *αα*-diphenyl-β-trinitrophenylhydrazine, $\text{NPh}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$, long prisms, m. p. 172—173° (decomp.), which is reduced by stannous chloride and hydrogen chloride in the presence of ether to diphenylamine and tetra-aminobenzene. When dissolved in dry chloroform it is oxidised readily by lead peroxide in the presence of anhydrous sodium sulphate to *αα*-diphenyl-β-trinitrophenylhydrazyl, violet-black prisms which show a remarkable resemblance to potassium permanganate. The substance dissolves in all media with the formation of violet solutions similar to those of permanganate; the colour of these shows no diminution in intensity when they are cooled in a mixture of ether and carbon dioxide, thus showing the degree of dissociation to remain unchanged at this low temperature. The solutions are, in general, remarkably stable, but decomposition occurs slowly when they are exposed to direct sunlight. The radicle converts quinol into quinone and is itself reduced to *αα*-diphenyl-β-trinitrophenylhydrazine, the change in colour being so sharp that solutions of the hydrazyl can be titrated with standard quinol solutions.

The hydrazyl reacts very readily with bromine in chloroform solution, giving the substance, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$, slender needles, m. p. 179—180° (decomp.) after previous softening; the constitution of the compound follows from the observations that it can be oxidised to a radicle and that it is reduced to tetra-aminobenzene and bromodiphenylamine, colourless needles, m. p. 64°.

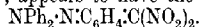
In contrast to other radicles containing bivalent nitrogen, the hydrazyl does not unite with nitric oxide. It reacts with tetraphenylhydrazine in boiling toluene (under these conditions the latter suffers incipient dissociation); the product, however, is not formed by the expected union of the radicles. The hydrazyl behaves as a dehydrogenating agent, being itself converted into the corresponding hydrazine and transforming the tetraphenylhydrazine into 5:10-diphenyldihydrophenazine, $\text{C}_6\text{H}_4\cdot\begin{smallmatrix} \text{NPh} \\ \text{NPh} \end{smallmatrix}\cdot\text{C}_6\text{H}_4$, m. p. 169—174°. It exerts a similar action towards amines and phenols, but the products have not been investigated closely.

Diphenyltrinitrophenylhydrazyl and triphenylmethyl give a compound, $\text{C}_{37}\text{H}_{27}\text{O}_6\text{N}_5$, short, yellowish-red prisms, m. p. (indefinite) 182—183° (decomp.); which cannot have the expected constitution, $\text{NPh}_2\cdot\text{N}(\text{CPh}_3)\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$, since it is readily oxidised to a violet radicle. It is therefore assumed that wandering of the triphenylmethyl group has occurred (cf. Wieland, A., 1919, i, 324) with the production of the compound, $\text{CPh}_3\cdot\text{C}_6\text{H}_4\cdot\text{NPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$. Simultaneously, dehydrogenation of the triphenylmethyl must have taken place, since a considerable proportion of the hydrazyl is recovered as hydrazine; this side of the reaction has not been investigated completely.

Diphenyltrinitrophenylhydrazyl, dissolved in benzene, reacts

readily with nitrogen peroxide, yielding β -hydroxy- $\alpha\alpha$ -diphenyl-3-trinitrophenylhydrazine, $\text{NPh}_2\cdot\text{N}(\text{OH})\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$, large, red crystals with a bluish-black glance, m. p. (indefinite) $156-157^\circ$ (decomp.), after softening and darkening at 145° . The course of the change is probably represented by the scheme $\text{NPh}_2\cdot\text{N}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3 \xrightarrow{\text{NO}_2} \text{NPh}_2\cdot\text{N}(\text{O}\cdot\text{N}\cdot\text{O})\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3 \xrightarrow{\text{H}_2\text{O}} \text{NPh}_2\cdot\text{N}(\text{OH})\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$. The constitution assigned to the compound is based on the following observations. It is an acid which dissolves in sodium carbonate to a red solution; it does not yield diphenylamine, tetra-aminobenzene, or *p*-hydroxydiphenylamine when reduced. It is oxidised by lead peroxide to a substance, $\text{C}_{18}\text{H}_{12}\text{O}_7\text{N}_5$, short, blackish-green prisms, m. p. 198° (decomp.), which gives red solutions in organic media. Since it reacts only slowly and gradually with bromine, the substance is regarded as a radicle containing quadrivalent nitrogen, $\text{NPh}_2\cdot\text{N}(\text{O})\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$. The investigation of the substance is, however, not yet concluded. H. W.

Amine-oxidation. V. Action of Tetranitromethane on Triphenylhydrazine. STEFAN GOLDSCHMIDT and KONRAD REXY (*Ber.*, 1922, 55, [B], 644-647).—In the hope of obtaining well-crystallised additive compounds of triarylhydrazines, the action of tetranitromethane on triphenylhydrazine dissolved in anhydrous ether has been investigated; the product, bluish-green, lustrous leaflets, decomp. 107° , appears to have the constitution,



It liberates two atomic proportions of iodine from acidified potassium iodide solution and thereby becomes reduced to the leuco-compound, $\text{C}_{18}\text{H}_{15}\text{O}_4\text{N}_4$, colourless crystals, m. p. 85° (decomp.), after darkening at 75° , in a capillary tube filled with carbon dioxide; the latter substance is isolated by reduction of an ethereal solution of the primary compound with zinc dust and glacial acetic acid. More drastic reduction of the quinone with stannous chloride gives diphenylamine and the compound $\text{NPh}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$, yellow crystals, m. p. 175° . The position of the $\text{C}(\text{NO}_2)_2$ group is not established definitely. H. W.

Action of Mercuric Acetate on certain Aminoazo-compounds. L. VECCHIOTTI (*Gazzetta*, 1922, 52, i, 137-139).—The interaction of mercuric acetate and aminoazobenzene in aqueous alcoholic solution yields the brown compound, $\text{C}_{12}\text{H}_{10}\text{N}_3\cdot\text{Hg}\cdot\text{OAc}$, m. p. 174° , which blackens and decomposes in light.

The action of mercuric acetate on chrysoidine under similar conditions yields: (1) *Dimercuridiaminoazobenzene diacetate*, $\text{C}_{12}\text{H}_{10}\text{N}_4(\text{Hg}\cdot\text{OAc})_2$, which crystallises in violet-red scales, m. p. 186° . (2) *Monomercuridiaminoazobenzene acetate*, $\text{C}_{12}\text{H}_{11}\text{N}_4\cdot\text{Hg}\cdot\text{OAc}$, which forms an orange-red powder, m. p. 165° . (3) The compound $(\text{C}_{12}\text{H}_{11}\text{N}_4)_2\text{Hg}$, which crystallises in dark red needles, m. p. 110° . T. H. P.

Mobility of Protein Ions. WOLFGANG PAULI (*Biochem. Z.*, 1922, 127, 150-155).—Potentiometric experiments on the chlorides

of basic proteins at constant temperature show that the mobility of the protein cation increases to a maximum with increasing concentration of the acid added, due to an increase in the equivalence of the protein ion. This applies to horse serum-albumin, gluten, and glucose. For acidic proteins, casein, globulin, fibrin, which form neutral salts with alkali, conductivity measurements are applicable. Casein forms a trivalent and globulin a quadrivalent anion.

H. K.

Are the Carbohydrate Groups which appear in the Acid Hydrolysis of Blood Globulin a Fission Product of the Protein Molecule? LEO LANGSTEIN (*Biochem. Z.*, 1922, **127**, 34—37).—Carefully purified globulin on hydrolysis by dilute sulphuric or hydrobromic acid gives between 0.5 and 1% of reducing substances with a positive fermentation test. The carbohydrate is considered to be an essential constituent of the globulin molecule.

H. K.

Casein from Cow's Milk. B. BLEYER and R. SEIDL (*Biochem. Z.*, 1922, **128**, 48—75).—A comparison has been made of two specially purified caseins, one prepared by the action of lactic acid on milk and the other by the action of rennin. The acid-casein contained 15.5% N and rennin-casein 15.64%. The equivalent weight of both caseins was 1145 when neutralised to phenolphthalein by alkali hydroxides, ammonia, or alkaline-earth hydroxides. When excess of the two caseins was shaken with increasing amounts of calcium, strontium, or barium hydroxides at constant temperature, the ratio of the alkali taken up by the caseins to the amount left free in the solution was a constant (Henry's law). When shaken with increasing content ($N/2500$ to $N/100$) of hydrochloric, sulphuric, lactic, or acetic acid the rennin-casein absorbed more of each of the acids than the acid-casein. Henry's law was obeyed for the highest dilutions of acids, but at higher concentrations the relation is one of adsorption.

H. K.

The Thermostable Active Agent of Pig's Pancreas. WALTER JONES (*J. Biol. Chem.*, 1922, **50**, 323—328).—Evidence is now adduced to show that hydrolysis of yeast-nucleic acid into its nucleotides by boiled pancreas extract (A., 1920, i, 687) does not produce any increase in the titratable acidity of the solution, although addition of adenine nucleotide to the digested solution increases the titratable acidity by an amount which agrees with that calculated from the weight added. Levene's criticism (A., 1921, i, 821) of the author's formula for yeast-nucleic acid can, therefore, no longer be maintained.

E. S.

Histopeptone. K. FELIX (*Z. physiol. Chem.*, 1922, **119**, 66—71).—Histopeptone is a homogeneous substance. The figures obtained for the hexone bases agree with those obtained by Kossel. No new substances could be obtained by fractionating the peptone by "salting out" or by precipitation by the silver-baryta method at different hydrogen-ion concentrations.

S. S. Z.

The Action of Pepsin and Trypsin on Diastase. W. BIEDER-
MANN (*Biochem. Z.*, 1922, **127**, 38—46).—Experiments with salivary
diastase show that the enzyme is destroyed by pepsin, but not by
trypsin. H. K.

Asymmetric Syntheses by means of Enzyme Action. IV.
L. ROSENTHALER (*Fermentforsch.*, 1922, **5**, 334—341; cf. A., 1909,
i, 74, 622; 1910, i, 603).—A dextrorotatory nitrile is obtained by
the action of hydrocyanic acid in the presence of emulsin on citron-
ellal, isovaleraldehyde, or *p*-tolualdehyde, whereas *o*-chlorobenz-
aldehyde gives a dextrorotatory product. The nitrile obtained
from *o*-methoxysalicylaldehyde, benzoyl-*o*-methoxysalicylaldehyde,
or benzoylvanillin is optically inactive.

The optical activity of the products obtained from isovaler-
aldehyde, heptaldehyde, benzaldehyde, anisaldehyde, cinnam-
aldehyde, citral, or citronellal attains a maximum value after a
given interval of time and subsequently diminishes; the rates of
increment and decrement vary greatly with the different aldehydes.

The possibility that emulsin not only catalytically accelerates the
formation of nitrile but also causes a displacement of the equilibrium
towards the nitrile side has been discussed previously; with acet-
aldehyde and isobutaldehyde, this displacement is not very marked,
whereas with benzaldehyde the results are not uniform, although in
one instance a pronounced displacement was observed.

The addition of hydrocyanic acid to acetaldehyde, isobutalde-
hyde, and benzaldehyde is a reaction of the second order; in the
presence of emulsin this is not strictly the case, since the "con-
stants" generally diminish regularly, thus indicating a consump-
tion or inactivation of the catalyst (cf. Nordefeldt, this vol., i, 66).
The action of hydrocyanic acid on acetaldehyde, isobutaldehyde,
benzaldehyde, anisaldehyde, or *o*-nitrobenzaldehyde in the presence
of sodium hydroxide is termolecular, but the mode of action of the
alkali hydroxide has not yet been elucidated. H. W.

Carboligase. III. CARL NEUBERG and HEINZ OHLE (*Biochem.*
Z., 1922, **127**, 327—339; cf. A., 1921, i, 480; this vol., i, 305).—
The product arising from benzaldehyde and pyruvic acid under
the influence of carboligase has now been shown to have the consti-
tution $l\text{-OH-CHPh-CO-CH}_3$. On treatment with magnesium phenyl
bromide, it gives *d*- $\alpha\beta$ -dihydroxy- $\alpha\beta$ -diphenylpropane, m. p. 83—84°,
 $[\alpha]_D^{25} + 45.1^\circ$ in alcohol, $+31.85^\circ$ in acetone (cf. McKenzie and
Wren, T., 1910, **97**, 473). Further treatment with dilute sulphuric
acid gave α -methyldeoxybenzoin. The racemic substances,
 OH-CHPh-CO-CH_3 and $\text{Ph-CO-CH(CH}_3\text{)-OH}$, stated to have been
synthesised by previous workers, are now shown to be the same
substance, probably an equilibrium mixture of the two. H. K.

Artificial Zymogens. II. MARTIN JACOBY (*Biochem. Z.*,
1922, **128**, 80—88; cf. A., 1920, i, 690).—More nickel is taken up
by a urease solution than by water, as is indicated by Tschugaev's
test. The longer a urease solution is kept in contact with nickel
powder or nickel oxide, the greater is the falling off of enzymic activity

due to formation of artificial zymogen. The filtrates from such solutions are restored to their original or slightly greater activity by potassium cyanide. H. K.

Artificial Zymogens. III. MARTIN JACOBY and T. SHIMIZU (*Biochem. Z.*, 1922, **128**, 89—94).—Metallic nickel, cobalt, copper, and zinc inactivate urease, but iron is without action. Cobalt, copper, and zinc act more quickly than nickel, and in the case of cobalt and copper, the quantity of artificial zymogen which can be reactivated by potassium cyanide or glycine falls off rapidly with time. H. K.

Artificial Zymogens. IV. Inactivation and Reactivation of Takadiastase. MARTIN JACOBY and T. SHIMIZU (*Biochem. Z.*, 1922, **128**, 95—99).—Diastase solution is not inactivated by contact with metallic iron, nickel, copper, or cobalt. Inactivation by mercuric chloride is temporary, being restored by potassium cyanide. H. K.

Adsorption of Ferments and Zymogens. I and II. MARTIN JACOBY and T. SHIMIZU (*Biochem. Z.*, 1922, **128**, 100—102, 103—107).—I. Tribasic calcium phosphate partly adsorbs urease, but does so more completely in the presence of electrolytes. Urease inactivated by nickel or cobalt is completely adsorbed and is reactivated by potassium cyanide. Dibasic calcium phosphate has no action.

II.—Urease solution treated with an alcoholic solution of cholesterol and filtered loses activity, the precipitate being very slightly active and the filtrate slightly active, but having its activity restored by glycine or serum. An inactivated urease (by nickel), when treated with cholesterol and filtered, passes unchanged into the filtrate and is reactivated by glycine or potassium cyanide. H. K.

The Influence of Cobaltamines on the Action of Catalase and Amylase. EBERHARD FUNK (*Biochem. Z.*, 1922, **128**, 108—118).—Hexamminecobaltic chloride, nitropentamminecobaltic chloride, dinitrotetramminecobaltic chloride, trinitrotriamminecobalt, potassium tetranitrodiamminecobaltate, and sodium cobaltinitrite inhibit the action of catalase, the inhibition increasing with decrease in the number of ammonia groups. In the presence of a phosphate buffer, P_H about 7, the earlier members of the series no longer inhibit. Unlike catalase, amylase (takadiastase) has its action accelerated by this series of complex salts. H. K.

Preparation of Derivatives of 3 : 3'-Diamino-4 : 4'-dihydroxyarsenobenzene. GEORG SPEYER-HAUS (Brit. Pat. 155577).—Derivatives of salvarsan which are stable in aqueous solution are obtained by dissolving together equal weights of the methylene sulphoxylate of 3 : 3'-diamino-4 : 4'-dihydroxyarsenobenzene and its sodium salt or the complex silver compound of the sodium salt. That new chemical compounds are thereby formed is proved by the fact that the resulting solutions no longer give precipitates with

carbon dioxide, and the silver solution gives no precipitate with sodium chloride. The solutions keep unchanged for many hours without formation of any precipitate or increase in toxicity or any loss of therapeutic activity.

G. F. M.

Aromatic Compounds of Antimony. V. Differing Behaviour of Lithium Hydroxide from that of Sodium or Potassium Hydroxide in the Hydration of Polymeric Arylstibinic Acids. HANS SCHMIDT (*Ber.*, 1922, 55, [B], 697—701; cf. A., 1920, i, 900).—It has been shown previously that a solution of trimeric phenylstibinic acid appears to be neutralised initially by one molecular proportion of sodium hydroxide (indicator, phenolphthalein) but that in course of time further quantities of alkali hydroxide are required until, finally, nearly three molecular proportions have been added. The phenomenon has been regarded as a fission of the trimeric to the monomeric form. Potassium hydroxide resembles sodium hydroxide in its behaviour, but the acid appears capable of neutralising only a markedly smaller proportion of lithium hydroxide, with which hydration seems only to proceed to the dimeric stage: $(\text{PhSbO}_2)_3 = (\text{PhSbO}_2)_2 + \text{PhSbO}_2$. *p*-Aminophenylstibinic acid resembles the parent acid closely in its behaviour. On the other hand, *p*-chloro-, *m*-nitro-, and *p*-chloro-*m*-nitro-phenylstibinic acids are hydrated by lithium hydroxide in the same manner as by sodium hydroxide. A satisfactory explanation of the differing behaviour of the various alkali hydroxides cannot at present be given.

H. W.

Physiological Chemistry.

Comparative Investigations on the Blood Sugar Content of the Arterial and Venous Vascular Systems. KARL TURBAN (*Z. physiol. Chem.*, 1922, 119, 4—10).—The sugar content of the arterial and venous blood of starving and fed dogs was studied. Generally the arterial blood showed a higher sugar content than venous blood.

S. S. Z.

Blood Sugar. I. A Critical Survey of the Methods of Estimation of Blood Sugar and of the "Threshold" Concept. MAX ROSENBERG (*Arch. exp. Path. Pharm.*, 1922, 92, 153—164).—The methods dealt with are those of Bang and of Bertrand. The sources of error are considered and stress is laid on the importance of making the estimations under basal physiological conditions, and on the advisability of estimating the sugar of the plasma rather than that of the whole blood.

From a consideration of the available literature the author concludes that the threshold value is not a constant in any individual, but varies with the physiological needs of the organism as a whole.

C. R. H.

Influence of Amino-acids and Fatty Acids on the Regulation of the Blood Sugar. LEO POLLAK (*Biochem. Z.*, 1922, **127**, 120—136).—Subcutaneous injection into normal rabbits of 1 gram of glycine, alanine, or asparagine produced hyperglycaemia, as also does Witte peptone, but not leucine. Hyperglycaemia is also produced by saturated fatty acids with an uneven number of carbon atoms, those with an even number being inactive. Previous or simultaneous injection of ergotamine (Sandoz) completely inhibits the hyperglycaemia. The effect is in each case attributed to mobilisation of glycogen due to stimulation of the sympathetic nerve-endings. H. K.

The Ammonia Content of Blood. THOMAS P. NASH, jun., and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1922, **51**, 183—185).—Further experiments are described confirming the conclusion that ammonia is formed by the kidney (cf. this vol., i, 191). E. S.

The Amino-acid Nitrogen Content of the Blood. SEIZABURO OKADA and TOWORU HAYASHI (*J. Biol. Chem.*, 1922, **51**, 121—133).—Estimations were made of the amino-acid nitrogen content of the blood in certain pathological cases, and in animals under experimental conditions. No increase was observed following subcutaneous injection of adrenaline or pituitrin or removal of the thyroid gland. Increases were, however, observed after injection of pilocarpine and after removal of the kidneys, whilst complete removal of the pancreas produced a transient rise. The amino-acid content of human blood varies with the number of white corpuscles, in which the amino-acids appear to be concentrated. It is suggested that the nuclei are responsible for this concentration. E. S.

The Effect of Carbon Monoxide, Illuminating Gas, and Benzene on Blood Coagulation Time. H. S. FORBES and LOUISE HOMPE (*J. Ind. Hyg.*, 1921, **3**, 213—216).—Experiments showed no constant change of coagulation time in the blood of cats gassed with these gases. The prothrombin content of the blood was unaltered; there was no evidence of hæmolytic or of blood destruction. The condition of coma found in fatal human cases of illuminating gas poisoning could not be duplicated in cats. They died in the gas or recovered entirely. CHEMICAL ABSTRACTS.

Separate Analyses of the Corpuscles and the Plasma. HSIEN WU (*J. Biol. Chem.*, 1922, **51**, 21—31).—The system of blood analysis developed by Folin and Wu (*A.*, 1919, ii, 308; *A.*, 1920, ii, 337) may be applied to the corpuscles and plasma separately. From the results of analyses of normal human blood the following approximate ratios, representing the concentration in the plasma to that in the corpuscles, are given for the various constituents: urea 1 : 1, sugar 1 : 1, uric acid 2 : 1, chloride 2 : 1, amino-acids 1 : 2. Creatine is practically absent from the plasma, whilst undetermined non-amino-nitrogen, which, it is suggested, represents peptides and peptones, is confined almost entirely to

the corpuscles. These and other results indicate the desirability of substituting plasma analysis for whole blood analysis. E. S.

Fixation of Quinine by Corpuscles and its Action on Cell Respiration. P. RONA and E. BLOCH (*Biochem. Z.*, 1922, 128, 169—184; cf. A., 1922, i, 65).—The red blood-corpuscles of birds and of mammals are permeable to quinine and its salts, but yeast-cells are only permeable to quinine. On the respiration of corpuscles, the base alone has an inhibitory action, the first effect being to accelerate respiration, followed by inhibition of respiration until an equilibrium is reached where the respiration attains a constant value with time. At this point the inhibition is proportional to the concentration of the quinine. H. K.

The Non-haemoglobin Nitrogen Content of Corpuscles, a Contribution to the Nitrogen-metabolism of Tissues. RUDOLF SCHOEN (*Biochem. Z.*, 1922, 128, 293—309).—The author has estimated the nitrogen content, by Bang's micro-Kjeldahl method of analysis, of washed and defibrinated blood-corpuscles of normal and pathological cases. The haemoglobin content, the volume, and the number of the corpuscles have been estimated simultaneously. As the nitrogen content of haemoglobin is known, an approximate value for the non-haemoglobin nitrogen can be obtained. For normal men, one million corpuscles contain 0.00563 mg. of nitrogen, for women 0.00527. The value is not subject to much variation. H. K.

The Glycogen Content of White Blood-corpuscles. J. DE HAAN (*Biochem. Z.*, 1922, 128, 124—143).—By means of a micro-method for the estimation of glycogen depending on the use of Plüger's method and Bang's method for the estimation of the dextrose produced on hydrolysis, the author has examined the glycogen content of the leucocytes with special reference to their iodophilic properties. The glycogen content of leucocytes from serous exudates from rabbits and goats is between 1 and 2%, and is uninfluenced by injections of starch or dextrose. In vitro, however, the glycogen content of leucocytes quickly falls off, due probably to lysis, unless fixed by some reagent, when it becomes resistant to diastase. The normal leucocytes of the blood of the horse and of the pig contain about 1% of glycogen, which is the sole glycogen in the blood. H. K.

Comparison of the Viscosity and Velocity of Ultra-filtration of Serum. ALEXANDER ELLINGER and S. M. NEUSCHLOSZ (*Biochem. Z.*, 1922, 127, 241—254).—A comparison of the relative viscosities of serum-Ringer solution mixtures and their relative velocities of ultra-filtration shows a relationship to exist but no exact inverse proportionality. With increasing P_H of the solution, the velocity of ultra-filtration falls off and the viscosity increases. Anions increase the viscosity of inactivated horse-serum in the order citrate > sulphate > acetate > Cl > Br > I > SCN. The presence of small quantities of caffeine may raise or depress the viscosity, depending on the P_H of the solution. H. K.

Water and Ionic Distribution in the Organism. HEINRICH REICHEL (*Biochem. Z.*, 1922, **127**, 322–326).—The change of colour of a dialysed serum solution containing methyl-orange on addition of sodium chloride is attributed to a new distribution of the indicator between what the author regards as practically anhydrous emulsoid phase and the aqueous solution. H. K.

The Influence of Radiations on the Hydrolysis of Fats. LUDWIG PINCUSSEN and J. L. ANAGNOSTU (*Biochem. Z.*, 1922, **128**, 268–273).—Butyric or tributyrin in aqueous solution, exposed to the light of an arc or incandescent lamp, with or without the addition of sensitising dyes (eosin or methylene-blue) are unchanged, as is shown by measurements with the viscostalagmometer. The hydrolytic action of normal rabbit's serum on butyric or tributyrin falls off slightly on exposure to an incandescent lamp, but is unchanged under Röntgen radiation. Experiments on exposure of rabbits to various sources of radiation are interpreted in a somewhat similar manner. H. K.

Distribution of Enzymes in the Alimentary Canal of the Chicken. ROBERT HENRY ADERS PLIMMER and JOHN LEWIS ROSEDALE (*Biochem. J.*, 1922, **16**, 23–26).—In the crop of the chicken diastase, lactase, and a weak peptic enzyme are present; in the proventriculus, a peptic enzyme; in the pancreas, diastase, lipase, and proteoclastic enzymes which act in neutral, acid, and, particularly, alkaline media; in the whole intestine, invertase, diastase, and peptic and tryptic enzymes; in the duodenum, peptic and tryptic enzymes; and in the caeca, diastase.

W. O. K.

Intestinal Saccharase. E. KNAEFL-LENZ (*Z. physiol. Chem.*, 1922, **119**, 60–65).—The surviving intestine of the rabbit can invert sucrose. The inversion velocity is of the same order of magnitude as that obtained by Euler and Svanberg with minced pig's intestine. The inversion velocity is one-half the normal after the intestine is irrigated, which shows that the enzyme is secreted by the cells in the intestine.

S. S. Z.

The Rôle of Acid in Carbohydrate Metabolism. V. The Action of Acid and Alkali on the Carbohydrate Metabolism of Yeast-cells. H. ELIAS and ST. WEISS (*Biochem. Z.*, 1922, **127**, 1–12).—By treatment with acid, the glycogen content of yeast-cells remains unaltered, but with alkali the glycogen increases and at higher concentrations of alkali passes into the surrounding fluid. The increase of glycogen is not at the expense of the sugar, but of protein, as is demonstrated by the increase in non-precipitable nitrogen.

H. K.

Carbohydrate Metabolism. III. A Study of Urinary Sugar Excretion in Twenty-six Individuals. ISAAC NEWWIRTH (*J. Biol. Chem.*, 1922, **51**, 11–16).—An extension of work previously described (Benedict, Osterberg, and Newwirth, A., 1918, i, 322) to a larger number of individuals.

E. S.

The Relations between Fats and Carbohydrates. HASS MÜLLER (*Helv. Chim. Acta*, 1922, 5, 163—166).—Whilst much light is thrown on the metabolic relationships of carbohydrates to proteins by the interconversions of alanine and lactic acid (Neuberg and Langstein, *Arch. Anat. Physiol.*, 1913, *Suppl.*, 514; Embden and others, *A.*, 1911, ii, 53; 1912, ii, 278, 279), less is known in regard to the fats, which mostly contain an even number of carbon atoms, and of which β -oxidation furnishes only compounds containing two carbon atoms. It is probable, however, that β -oxidation may occur (Spiro, this vol., i, 489) furnishing, for example, succinic and butyric acids. The organism contains an oxydase by which succinic acid can be converted into fumaric acid (Battelli and Stern, *A.*, 1911, ii, 132); the latter has been detected in fresh meat (Einbeck, *A.*, 1914, i, 773) and is now stated rapidly to furnish carbon dioxide and lactic acid when its sodium salt is treated with fresh yeast. This observation explains the "gluconeogeny" arising from succinic and fumaric acids (Cremer, *Berl. klin. Woch.*, 1913, 50, 1457). The formation of lactic acid from succinic acid is to some extent analogous to that of acetone from butyric acid. Since acetone may also be produced from proteins (Friedmann, *A.*, 1908, ii, 719; 1913, i, 1277), and succinic acid is an oxidation product of glutamic acid (Neuberg and Ringer, *A.*, 1915, i, 1046), the question arises as to whether the above observations are not applicable to the question of protein metabolism. J. K.

The Biological Difference of Stereoisomerides. A. JUNG and H. MÜLLER (*Helv. Chim. Acta*, 1922, 5, 239—243).—Fumaric acid, but not its stereoisomeride, maleic acid, can give rise to "gluconeogeny" (Cremer, *Berlin. klin. Woch.*, 1913, 50, 1457). Further, the formation of lactic acid (into which fumaric acid is convertible by a carboxylase in yeast), in the organism of starving dogs suffering from phosphorus poisoning is suppressed in favour of gluconeogeny by administration of phlorrhizin. The connexion between the conversion of fumaric acid into lactic acid and gluconeogeny is borne out by the fact that yeast has no action on maleic acid. This, rather than their relative toxicities (Cremer, *loc. cit.*), is the cause of their different gluconeogenetic properties. Further, it is shown that whilst fumaric acid facilitates fermentation, maleic acid inhibits it. Maleic acid is fermented even more rapidly than fumaric acid, a fact which supports the view, arrived at from other considerations, that the latter, rather than the former, represents the primary product of the metabolism of succinic acid. The fact that β -hydroxybutyric acid is easily fermented whilst crotonic acid is unchanged points to the same conclusion. Acrylic and cinnamic acids are unaffected by yeast. J. K.

Reductions and Oxidations and a Coupled Reaction in the Intermediary Metabolism of the Animal Body. F. KNOOP (*Biochem. Z.*, 1922, 127, 200—209).—When α -amino- γ -phenylbutyric acid was administered orally to a dog, the *N*-acetyl derivative was excreted in the urine in proportionate amount.

If there be administered simultaneously pyruvic, butyric, or acetic acid the increase of acetylated product is respectively 50%, 18%, nil. Pyruvic acid is therefore the acetylating agent of the body. The amino-acid is oxidised to an imino-acid which combines with loss of carbon dioxide to yield the acetyl derivative of the amino-acid.

H. K.

Observations on Sugar Synthesis. I. J. K. PARNAS and RICHARD WAGNER (*Biochem. Z.*, 1922, **127**, 55—65).—A nine-year-old girl with a liver tumour had an abnormal sugar metabolism as indicated by negligible content of sugar in the blood after a fast (morning) and a urine rich in acetone. After a meal rich in carbohydrate the blood sugar rose to as high as 0.4%. This lasted a considerable time with absence of ketonuria, but with pronounced glycosuria. Administration of adrenaline showed no effect on the normal sugar content, but feeding with the following, proteins, glycine, alanine, glutamic acid, calcium lactate, caused an increase of sugar in the blood to about 0.1%. Administration of fats in the aglycæmic condition failed to produce sugar in the blood.

H. K.

Metabolism of Sulphur. IV. The Oxidation of Cystine in the Animal Organism. HOWARD B. LEWIS and LUCIE F. ROOT (*J. Biol. Chem.*, 1922, **50**, 303—310).—The administration of phenylcarbamido-cystine, both orally and subcutaneously, to rabbits was found to produce an increase in the unoxidised sulphur content of the urine. Using cystine under the same conditions, no such increase was observed, the sulphur in this case being eliminated as sulphate. Protection of the amino-group thus prevents oxidation of the cystine molecule, a result which indicates that deamination precedes, or is connected with, oxidation of the sulphur. A slight increase in the sulphate content of the urine which was observed after oral administration of phenylcarbamido-cystine is attributed to bacterial action.

E. S.

The Transportation, Retention, and Excretion of Carbohydrates. OTTO FOLIN and HILDEG BERGLUND (*J. Biol. Chem.*, 1922, **51**, 213—273).—A critical review of the more important literature of the subject is given. In the experiments performed, estimations were made of the sugar content of blood and urine after ingestion of various carbohydrates. Lower values than those given by other investigators were obtained for blood sugar, a result which is attributed to the absence from the subjects employed of emotional complications. With the exception of one case of renal glycosuria (subnormal renal threshold), and in the absence of emotional hyperglycæmia, no glycosuria was obtained after the ingestion of pure dextrose in amounts up to 200 grams. Following every ordinary carbohydrate meal, however, a definite glycosuria (Benedict, Osterberg, and Neuwirth, A., 1918, i, 322) was obtained, which was found to be independent of the level of blood sugar. This, apparently, is due to the absorption and excretion of sugars other than dextrose and lævulose, of unusable

materials present in food or produced from it during preparation, and to products of endogenous metabolism. The sugar of normal urine thus consists of a variety of carbohydrate products and derivatives.

A renal threshold analogous to, but independent of, that of dextrose exists for laevulose, but not for galactose or lactose. The utilisation of galactose depends on the amount of dextrose available.

The failure of sugar to accumulate in the blood is considered to be due, in the first place, to absorption by the tissues rather than to glycogen formation. When the tissues are well supplied, the need for sugar transportation ceases. Hypoglycaemia is probably a reflection of this, and is thus a normal consequence of carbohydrate ingestion.

The distribution of blood sugar between plasma and corpuscles is almost uniform during fasting, but varies irregularly at other times. Hydrolysis usually diminishes the sugar content of the plasma and increases that of the corpuscles. The latter, therefore, probably contain polysaccharides. E. S.

The Value of Gelatin in Relation to the Nitrogen Requirements of Man. ROBERT ROBISON (*Biochem. J.*, 1922, 16, 111—130).—On a diet practically free from nitrogen, a certain minimum amount of nitrogen, derived from the tissues of the body, is used and excreted. If a diet otherwise equivalent but containing nitrogen in the form of gelatin be given there is a saving in the body-nitrogen so used. By feeding on diets containing, in the gelatin, 4.88 grams, 7.54 grams, and 12.00 grams of nitrogen per day, the author has found, after making certain allowances, a saving of between 11.9 and 15.9%, 0 and 5.3%, 8.1 and 14.7%, respectively, of the minimum body-nitrogen.

The ratio of the nitrogen balance (nitrogen intake minus nitrogen output in urine) to the creatinine nitrogen is found to be fairly constant, and to be equal to that ratio as determined by McCollum (*A.*, 1912, ii, 72) for the pig. W. O. K.

Conditions of Inactivation of the Accessory Food Factors. SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1922, 16, 42—48).—The accessory food factors in cod liver oil and in decitrated lemon juice are easily destroyed by ozone at the ordinary temperature, whereas autolysed yeast retains its activity under exposure to ozone. Passing air through decitrated lemon juice at the ordinary temperature, or through cod liver oil at 120°, destroys their active factors. Ultra-violet rays have no effect on the accessory food factors in the absence of air. The effect of boiling is apparently due to oxidation as the potency of decitrated lemon juice is not destroyed by boiling in an atmosphere of carbon dioxide. It also retains its activity to a very considerable extent after hydrolysis for five hours by 2N-hydrochloric acid in an atmosphere of carbon dioxide. W. O. K.

Calcium in Egg-shell Formation. G. D. BUCKNER, J. H. MARTIN, W. C. PIERCE, and A. M. PETER (*J. Biol. Chem.*, 1922, 51, 51—54).—The experiments described indicate that hens can

utilise calcium carbonate for the production both of egg-shell and bones, whilst tricalcium phosphate can be utilised for the latter purpose only.

E. S.

Chemistry of Normal and Abnormal Pregnancies. J. A. KILLIAN and CARL P. SHERWIN (*Amer. J. Obstet. Gynecol.*, 1921, 2, 6—16).—In nephritic toxemias there is an increase in the non-protein and urea nitrogen of the blood, and more than 50% of the non-protein nitrogen is in the form of urea nitrogen. In normal pregnancies the urea nitrogen amounts to about 44% of the non-protein nitrogen, and for both the values are low. Normally in pregnancy the uric acid, creatinine, chloride, and sugar concentrations of the blood are not changed as compared with non-pregnant women. The carbon dioxide-combining power of the blood plasma is slightly increased late in pregnancy. In pernicious vomiting and eclampsia the non-protein nitrogen is greatly increased but the urea nitrogen amounts to but 15 to 38% of the non-protein nitrogen. Urea acid is increased.

CHEMICAL ABSTRACTS.

Blood Chemistry in Normal and Abnormal Pregnancy. WM. E. CALDWELL and WM. G. LYLE (*Amer. J. Obstet. Gynecol.*, 1921, 2, 17—34).—Comparative values are given as follows:

	Non-protein N.	Urea N.	Creatinine.	Uric acid.	Ratio: Urea N: Non-protein N.
Non-pregnant	35 mg. or less	18 mg. or less	2 mg. or less	3 mg. or less	50%
Normal pregnancy	29.69	11.51	1.65	1.73	39%
Eclampsia and toxemia...	49.7	26	2.17	6.19	52%

CHEMICAL ABSTRACTS.

Lipoids of the Crystalline Lens. M. GOLDSCHMIDT (*Biochem. Z.*, 1922, 127, 210—213).—The dried and powdered crystalline lens of the human eye at various ages was extracted successively with alcohol, light petroleum, acetone, and benzene. The light petroleum fraction consisted of cholesterol. The alcohol-soluble fraction was separable into substances no longer soluble in alcohol, cholesterol, and a phosphatide. Graphs are given showing the variations in cholesterol, phosphatide, acetone-soluble substances, and benzene-soluble substances with age.

H. K.

The Cleavage Products of the Crystalline Lens. VOSHIZUMI HIRAKATA (*J. Biol. Chem.*, 1922, 51, 155—164).—The following percentages of amino-acids, calculated on the ash- and water-free substance, were isolated from the hydrolysis product of the crystalline lens of the ox: Alanine 4.7, valine 1.0, leucine 6.8, aspartic acid 1.4, glutamic acid 15.5, lysine 1.6, arginine 3.3, phenylalanine 1.9, tyrosine 4.5, proline 2.2, histidine 1.6. A positive test was obtained for tryptophan. Adenine, identified by the melting point of its picrate, was also present, but no other purine bases were isolated.

E. S.

Lyotrope Series and β -Oxidation. K. SPIRO (*Biochem. Z.*, 1922, 127, 299—311).—Experiments on the isolated frog's heart

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show that anions affect the action of potassium. Potassium combined with thiocyan-anion is more toxic than with chloridion and the latter more so than with acetanion. Calcium chloride inhibits the toxicity of potassium chloride but not that of potassium thiocyanate. The primary toxic action of methyl and ethyl alcohols on the frog's heart is equivalent, but whereas the action of ethyl alcohol can be inhibited by washing out, that of methyl alcohol is almost unaffected.

H. K.

Localisation of the Degradation of Fats in the Body. JULIUS BAER (*Biochem. Z.*, 1922, **127**, 275—285).—Injection of butyric acid into the lymph sac of frogs is followed by excretion of small quantities of acetoacetic acid. This acid and butyric acid are destroyed to a considerable extent by normal frogs and by frogs with extirpated livers. β -Hydroxybutyric acid is oxidised by both types of frogs to acetoacetic acid.

H. K.

Liver Function. III. Phenol Conjugation as Influenced by Liver Injury and Insufficiency. K. F. PELKAN and G. H. WHIPPLE (*J. Biol. Chem.*, 1922, **50**, 513—526; cf. this vol., i, 86).—Experiments on dogs in which *p*-cresol was ingested before and after injury to, or excision of, the liver, the percentage conjugation which occurred being estimated in each case, indicate that conjugation of phenols is a function of the liver and of no other organ.

E. S.

Oil from the Liver of *Acanthias vulgaris*. T. LEXOW (*Chem. Umschau*, 1922, **29**, 59—60).—The oil from the liver of *Acanthias vulgaris* is almost water-white and has a faint, not unpleasant odour. When kept at 15°, some stearin is deposited. The following numbers were obtained: d_{20}^{20} , 0.9125; acid number, nil; saponification number, 156.4; iodine number (Wijs), 110.1; unsaponifiable matter, 12.31%; fatty acids, 79.28%; glycerol, 8.18%. The fatty acids freed from unsaponifiable matter had m. p. 27.8°; acid number, 177.8; saponification number, 189.5; mean molecular weight, 296.1. The unsaponifiable matter is soft and crystalline: iodine number, 72.9; m. p. 61.3—85°. It is soluble in an equal weight of lukewarm alcohol and crystals are deposited at -5°. The cholesterol test is given, but the acetate melts under 100°. The presence of higher alcohols or of squalene is not indicated.

H. C. R.

Permeability of the Glomerulus Membrane for Stereoisomeric Sugars, with Special Reference to Galactose. H. J. HAMBURGER (*Biochem. Z.*, 1922, **128**, 185—206).—Perfusion experiments on the frog's kidney with the Hamburger-Brinkman modification of Ringer's solution (increased calcium content) and containing various hexoses and pentoses in solution showed that *l*-mannose, *l*-arabinose, *l*-glucose, *d*-mannose, *d*-glucoseamine, and *d*-arabinose passed through the membrane completely, whereas *d*-galactose, *l*-xylose, *d*-ribose, and *d*-xylose were partly retained and *d*-glucose completely. Whatever the concentration of *d*-galactose, about one-half is always retained, and about 30% of *l*-xylose.

The tentative explanation adopted is that in the case of partial retention of the sugar only one form, α or β , can pass the membrane and in the case of *d*-glucose, neither modification can pass. Experiments on the α - and β -glucosides are foreshadowed. H. K.

Change of Permeability with Special Reference to Stereoisomeric Sugars. H. J. HAMBURGER (*Biochem. Z.*, 1922, **128**, 207—214).—The author discusses the importance of calcium on the permeability of membranes, with special reference to the work of Clowes (A., 1916, i, 583) on the change of a water-oil emulsion under the influence of calcium ion from a continuous water phase to a continuous oil phase. The former would be permeable to glucose, the latter impermeable. This gives a picture of the glomerulus membrane, the permeability of which may be likewise influenced by increasing or decreasing amounts of calcium and also by other substances, for instance, phloridzin. H. K.

Physiology of the Glands. LIII. Function of the Spleen under Normal and Increased Oxygen Requirements. LEON ASHER and ERNST BERNET (*Biochem. Z.*, 1922, **128**, 251—267).—A comparison has been made of the daily excretion of ammonia and total nitrogen in the urine of normal rabbits with the excretion in the case of rabbits, (1) with extirpated spleen, (2) suffering from lack of oxygen (with artificial pneumothorax), (3) with extirpated spleen and suffering from lack of oxygen. Extirpation of the spleen causes an increased excretion of nitrogen which is still greater where the respiratory surface of the lungs is diminished. H. K.

The Function of the Thyroid Gland in the Regulation of Temperature and in the Metabolism of Fever. E. GRAFE and E. VON REDWITZ (*Z. physiol. Chem.*, 1922, **119**, 125—138).—The thyroid gland has no influence on the regulation of the body temperature of the dog or on the metabolic functions during fever in this animal. S. S. Z.

The Influence of the Thyroid Gland on Metabolism, with Special Reference to Heat-regulation. PAUL SCHENCK (*Arch. expt. Path. Pharm.*, 1922, **92**, 1—21).—A study of the respiratory quotient in starvation experiments with normal and thyroid-ectomised animals indicates that the effect of the thyroid hormone on metabolism is qualitative rather than quantitative. The author states that the metabolism-regulating hormone of the thyroid is free from protein and almost free from iodine. He regards the heat regulation during muscular rest as being brought about, not by direct nervous stimulation of the heat centre, but indirectly by means of the thyroid hormone, and possibly also by the hormones of the other ductless glands. C. R. H.

Tethelin—the Alleged Growth-controlling Substance of the Anterior Lobe of the Pituitary Gland. JACK CECIL DRUMMOND and ROBERT KEITH CANNAN (*Biochem. J.*, 1922, **16**, 53—59).—Tethelin, which Robertson (A., 1916, i, 350) claims to have

isolated from the anterior lobe of the pituitary gland, is apparently a mixture, chiefly of substances of the lipid class.

Robertson's deductions as to the effect of tethelin and of the anterior lobe of the pituitary on growth are not warranted.

W. O. K.

The Pharmacology of Cell Respiration. PHILIPP ELLINGER (*Z. physiol. Chem.*, 1922, **119**, 11—38).—The endocrine glands contain products of protein degradation which can support the respiratory function of the erythrocytes of the goose. The presence of specific substances could not be demonstrated in these tissues. Urea increases whilst quinine decreases the velocity of oxidation of the erythrocytes of the goose owing to the increase and decrease in the absorptive surface produced by the respective substances.

S. S. Z.

Change of Choline Content of the Frog's Musculature through Electric Stimulation. E. GEIGER and O. LOEWI (*Biochem. Z.*, 1922, **127**, 174—180).—Faradic stimulation of frog's muscle leads to an increased choline content as estimated by a slight modification of Reid Hunt's method. The source of choline is possibly hydrolysis of lecithin.

H. K.

Formation of Phosphoric Acid in the Contraction of Frog's Muscle. GUSTAV EMBDEN and HEINZ LAWACZEK (*Biochem. Z.*, 1922, **127**, 181—199; cf. A., 1921, i, 529).—A comparison of the free phosphoric acid content of the two gastrocnemius muscles of frogs, submitted to faradic stimulation for short but different lengths of time shows that the free phosphoric acid very readily disappears, re-forming lactacidogen.

H. K.

The Amino-acids of Flesh. The Diamino-acid Content of Rabbit, Chicken, Ox, Horse, Sheep, and Pig Muscle. JOHN LEWIS ROSEDALE (*Biochem. J.*, 1922, **16**, 27—30).—Estimations have been made by the Van Slyke method of the diamino-acid content of the flesh of the rabbit, chicken, ox, horse, sheep, and pig. The red meats show a higher lysine content than the white meats.

W. O. K.

Swelling Processes in Subcutaneous Tissues. P. MORAWITZ and G. DENECKE (*Biochem. Z.*, 1922, **127**, 47—54).—Agar tablets which have increased in weight up to 30% by immersion in serum or Ringer's solution, when introduced into the subcutaneous tissues of normal rabbits for twenty-four hours, lose in weight, but in the tissues of animals suffering from an artificial incipient edema there is a slight increase in weight. Attempts to explain this through change of P_H or osmotic pressure of the fluids were not successful.

H. K.

Synthesis of Amino-acids in Animal Organisms. I. Synthesis of Glycine and Glutamine in the Human Organism. GEORGE J. SHIPLE and CARL P. SHERWIN (*J. Amer. Chem. Soc.*, 1922, **44**, 618—624).—It has been shown that man will synthesise glycine at the expense of carbamide, as do the lower

animals. The synthesis of glutamine at the expense of carbamide nitrogen is now also demonstrated in the case of man. The two amino-acids may be built simultaneously as readily as either compound alone. The carbamide nitrogen dropped from about 75% of the total nitrogen to 28%, and during a portion of a certain day to 12%, whilst these amino-acids were being synthesised in the organism. After feeding a moderate dose of benzoic acid, glycine for its detoxication is built within six hours, but for the detoxication of a corresponding dose of phenylacetic acid a somewhat longer period of time is required for the synthesis of glutamine. W. G.

The Zinc Content of the Organs of the Rabbit and of some Vertebrates. GABRIEL BERTRAND and R. VLADESCO (*Bull. Soc. chim.*, 1922, [iv], 31, 268—272).—In continuation of previous work (A., 1921, i, 382, 907), the authors record the zinc content of numerous organs of the rabbit and of certain organs of other vertebrates, such as the calf, bullock, sheep, chicken, etc. In general, the organs of birds are richer in zinc than those of mammals or fish. In the case of mammals or fish, the large organs such as muscle, liver, heart, etc., contain, on an average, 20—40 mg. of zinc per kilo. of fresh substance, whilst in birds the figure is about double this amount. In hen's eggs the zinc is entirely in the yolk, the white and shell of the egg being devoid of this metal. W. G.

Vitamin Requirements of *Drosophila*. I. Vitamins-B and -C. ARTHUR WILLIAM BACOT and ARTHUR HARDEN (*Biochem. J.*, 1922, 16, 148—152).—The complete development of flies of the genus *Drosophila* requires the presence of vitamin-B, but not of vitamin-C, and of, at most, very small quantities of vitamin-A. W. O. K.

Occurrence of Manganese in the Tube and Tissues of *Mesochætopterus Taylora*, Potts, and in the Tube of *Chætopterus variopedatus*, Renier. CYRIL BERKELEY (*Biochem. J.*, 1922, 16, 70—77).—Manganese is found in considerable quantities in the tube (0.03—0.07%) and tissues (0.002—0.015%) of *Mesochætopterus Taylora*, and in the tube (0.4—0.6%) of *Chætopterus variopedatus*. It is probably to be regarded as a waste material and not of physiological importance. W. O. K.

Hæmotoxins from Parasitic Worms. BENJAMIN SCHWARTZ (*J. Agric. Research*, 1921, 22, 379—432).—Certain worms parasitic on animals contain substances toxic to blood. The body-fluid and extracts of *Ascaris lumbricoides* contain a hæmolytic agent which is thermostable and non-specific. It is not found in worms immediately after removal from the host, but appears in a few days after keeping them alive in vitro. A substance is found which inhibits coagulation, and also a substance causing agglutination, specific for rabbit blood-cells. Hæmolytic substances were found in other parasitic worms (*Ancylostoma caninum*, *Bostonium phlebotomum*, *Hæmonchus contortus*, *Trichuris depressuscula*, and *Thysanotoma actinoides*). Normal blood-serum may inhibit hæmolysis by these agents. G. W. R.

The Colouring Matter and Wax of the Blood Louse (*Schizoneura lanigera*). FR. N. SCHULZ (*Biochem. Z.*, 1922, 127, 112—119).—The woolly threads of wax which surround the blood louse (a parasite of apple trees) have been examined, as well as the red juice obtained on crushing the insects. The alcoholic extract containing wax and colouring matter shows the spectrum and some reactions of cochineal contaminated by a second colouring matter, possibly a lipochrome. The wax, when purified, crystallises readily, has m. p. 48—49°, and gives 7—10% of glycerol and 76% of fatty acid. The latter acid has m. p. 36°, solidifies very readily, has a molecular weight 327, and has probably 20—22 carbon atoms in a branched chain. H. K.

Do the Amino-acids occur in Cow's Milk? YOSHIZUMI HJIKATA (*J. Biol. Chem.*, 1922, 51, 165—170).—After removal of proteins and lactose from fresh cow's milk, derivatives of the following substances were isolated from the filtrate: lysine, arginine, histidine, guanine, adenine, choline. Evidence was also obtained of the presence of monoamino-acids. E. S.

The Effect Produced on the Composition of Milk by the Administration of certain Inorganic and Organic Substances. W. DENIS, WARREN R. SISSON, and MARTHA ALDRICH (*J. Biol. Chem.*, 1922, 50, 315—322).—The experiments were performed on goats and the substances investigated were urea and calcium chloride. Ingestion of the former increased the urea content of both the blood and milk, whilst ingestion of the latter increased the chloride, but had no effect on the calcium content of these fluids. Intravenous injection of calcium chloride did not produce any change in the calcium content of milk. E. S.

Fatty Acids of Butter. F. FROG and S. SCHMIDT-NIELSEN (*Biochem. Z.*, 1922, 127, 168—173).—Fractionation of the methyl and ethyl esters of the acids of butter fat prepared from the milk of cows fed on a standard mixed diet gave the following composition: acetic acid—a trace, butyric acid 3.4%, hexoic acid 3.3%, octoic acid 1.9%, decoic acid 3.0%, lauric acid 3.7%, myristic acid 12.9%, palmitic acid 20.8%, stearic acid 6.2%, oleic acid 27.0%, and unidentified acids 9.8%. Some of the unidentified acids probably arise from the feeding materials. H. K.

Effect of Loss of Carbon Dioxide on the Hydrogen-ion Concentration of Urine. E. K. MARSHALL, jun. (*J. Biol. Chem.*, 1922, 51, 3—10).—The escape of carbon dioxide from acid urines produces no great change in the hydrogen-ion concentration. With neutral, alkaline, or dilute urines, however, an appreciable decrease occurs unless precautions are taken to prevent the loss of carbon dioxide. E. S.

Carbonic Acid and Bicarbonate in Urine. JAMES L. GAMBLE (*J. Biol. Chem.*, 1922, 51, 295—310).—The content of free carbonic acid in urine is nearly constant; that of bicarbonate, however, varies inversely as the hydrogen-ion concentration. With increasing

acidity, there is consequently a rapid diminution in total carbonic acid. From these results the inference is drawn that the elimination of carbon dioxide in urine is determined by the carbon dioxide tension of blood plasma. Further, the reaction of urines more alkaline than P_H 7.0 is determined by the carbonic acid : bicarbonate ratio rather than by the ratio of the phosphates. E. S.

Acetaldehyde as a Constituent of Normal Urine. W. STEPP and R. FEULGEN (*Z. physiol. Chem.*, 1922, **119**, 72—73).—The presence of acetaldehyde in normal human urine was demonstrated by the dimethyldihydroresorcinol reaction. The Stepp and Fricke "silver method" showed a content of 0.3 mg. of acetaldehyde in 1 litre of the fluid. Precautions were taken to demonstrate that the acetaldehyde was not produced by the bacterial fermentation after collection and that the persons from whom the urine was derived did not consume any alcohol. S. S. Z.

The Presence of Pyruvic Acid in Normal and Diabetic Urines. ROBERT FRICKE (*Z. physiol. Chem.*, 1922, **119**, 39—45).—Appreciable quantities of pyruvic acid cannot be demonstrated in either normal or diabetic urines. S. S. Z.

Effect of Severe Muscular Work on the Composition of the Urine. JAMES ARGYLL CAMPBELL and THOMAS ARTHUR WEBSTER (*Biochem. J.*, 1922, **16**, 106—110).—The urine of a subject accustomed to do 67,500 kilogrammetres of work in five hours showed an increase in creatinine, undetermined nitrogen, neutral sulphur, and lactic acid when an attempt was made to do 100,000 kilogrammetres of work in five hours. Acetone substances were present during part of the experiment.

During such severe muscular work, the acidity and the ammonia and phosphate content are higher during the night than during the day; the sulphur is evenly distributed, and the total nitrogen is higher during the day than during the night, as found in a previous research (cf. Campbell and Webster, this vol., i, 197). W. O. K.

Distribution of the Nitrogenous Constituents of the Urine on Low Nitrogen Diets. ROBERT ROBISON (*Biochem. J.*, 1922, **16**, 131—133).—Estimations have been made of the urinary nitrogen (total, urea, ammonia, creatinine, uric acid) in the human being on a diet containing only about 0.3 gram of nitrogen per day. The results show agreement with those of Folin (A., 1905, ii, 183 and 268) and others. W. O. K.

Influence of Putrefaction Products on Cellular Metabolism.
II. **The Influence of Phenylacetic and Phenylpropionic Acids on the Distribution of Nitrogen in the Urine.** YOSHI-ZUMI HIRAKATA (*J. Biol. Chem.*, 1922, **51**, 141—154).—Phenylacetic and phenylpropionic acids, administered either orally or subcutaneously to rabbits, have the same effect on the excretion of nitrogen in the urine. With small doses, there is an increase in amino-acid and a slight decrease in urea whilst total nitrogen and ammonia remain unchanged. Larger doses produce an increase

in all four types of nitrogen both with fasting animals and with those maintained in nitrogen equilibrium. E. S.

Lævulosuria. HERMANN K. BARRENSCHEEN (*Biochem. Z.*, 1922, **127**, 222—230).—Examination of the metabolism of a case of lævulosuria (female aged twenty-two) showed that dextrose and galactose were utilised completely, as was white bread. When lævulose was given in a single dose, 10% passed into the urine independently of the dose; but where the administration was spread over a period, the excretion of lævulose was much greater. The blood sugar increased from 0.1 to 0.2% on oral administration of 50 grams of lævulose within forty-five minutes, falling off to normal in six and a half hours. H. K.

Acetonuria Produced by Diets containing Large Amounts of Fat. ROGER S. HUBBARD and FLOYD R. WRIGHT (*J. Biol. Chem.*, 1922, **50**, 361—402).—Experiments were made on a number of normal subjects to determine the effect of diets rich in fat on the excretion of acetone compounds. Using as a basis for calculation the conclusion reached by Shaffer (*A.*, 1921, **i**, 754) that the minimum molecular ratio of ketogenic to antiketogenic substance for the avoidance of ketonuria is unity, the authors conclude from their results that proteins and the glycerol portion of the fat molecule function as antiketogenic substances only to the extent that they produce dextrose in the organism. E. S.

A Case of Unusual Acetonuria. ORTO PORGES (*Biochem. Z.*, 1922, **127**, 293—298).—An account of a female patient who developed an acetonuria very rapidly after withdrawal of carbohydrate diet. H. K.

Reduction Reactions in the Urine of Patients treated with Arsenobenzenes. A. GAVIATI and T. PAVOLINI (*Arch. Farm. speriment. Sci. aff.*, 1921, **32**, 1—10, 17—26).—Aqueous solutions of arsenobenzene derivatives readily reduce alkaline bismuth and copper solutions. Solutions of these derivatives in urine reduce the bismuth solutions appreciably and the copper but slightly, respond to Abelin's test for amino-groups in all cases, and exhibit the presence of formaldehyde when the derivatives contain the aldehyde group. The reactions given by the urines of patients to whom arsenobenzene preparations have been administered by injection are, excepting in cases of glycosuria, mostly the expression of physico-chemical modifications produced in the urine and only occasionally due to the direct action of the preparations on the reagents. The administration of silver-salvarsan may be followed by transitory symptoms of albuminuria, glycosuria, and urobilinuria. T. H. P.

Bladder Calculus of Silicic Acid. A. SCHLICHT (*Pharm. Zeit.*, 1922, **29**, 316).—Stones found in the bladder of a wether were approximately spherical, of 1—6 mm. diameter, and very hard. The amount of organic matter was very small, the major portion of the mass consisting of silica. H. K.

Chemistry of Amyloid Degeneration. HANS EPPINGER (*Biochem. Z.*, 1922, **127**, 107—111).—An amyloid tumour of the liver proved to be protein in nature, but free from sulphur and phosphorus. It was rich in diamino-acids and in tyrosine, but cystine and histidine were absent as also were carbohydrates. H. K.

Zinc and Cancer. PAUL CRISTOL (*Compt. rend.*, 1922, **174**, 887—889).—An examination of the zinc content of benignant conjunctive tumours and malignant epithelial tumours show that the latter contain a much higher percentage of zinc than the former.

W. G.

Cancerous Anæmia. A. ROBIN and A. BOURNIGAULT (*Bull. acad. med.*, 1921, **85**, 198—203).—Estimations of the iron content of the blood and tissues of normal and cancerous individuals indicate that in the latter there is a considerable decrease in iron. Normal blood averages 0.439 gram; that of cancerous persons 0.257 gram, or a loss of 41%. In the tissues at the cancerous foci the difference in iron content amounts to 60%. Urinary elimination of iron in the non-cancerous averages 2.15 mg. as compared with 5.85 mg. for cancerous individuals.

CHEMICAL ABSTRACTS.

The Kidney Factor in Phloridzin Diabetes. THOMAS P. NASH, jun. (*J. Biol. Chem.*, 1922, **51**, 171—181).—In phloridzinised dogs there is a lower concentration of sugar in renal venous blood than in general arterial blood. These and other results indicate that phloridzin diabetes is not accompanied by an active production of sugar in the kidneys, and confirm an increased permeability of the renal epithelium.

E. S.

Composition of a Rhinolith. L. DEBUCQUET (*J. Pharm. Chim.*, 1922, **25**, 305—306).—A rhinolith, taken from the nasal chambers of a young soldier, contained 79.5% of calcium phosphate and 10.7% of calcium carbonate, the remainder being material insoluble in hydrochloric acid. It is of interest to note that the ratio of phosphate to carbonate is 7.43, a value which is very close to that for human bones.

W. G.

The Protein Requirement in Tuberculosis. WM. S. McCANN (*Arch. Int. Med.*, 1922, **29**, 33—58; cf. *ibid.*, 1921, **28**, 847).—In nine out of ten cases of tuberculosis, the minimum excretion of nitrogen was from 0.041 to 0.093 gram per kilo. per day; in the tenth case, in which the basal metabolism was 30% above normal, the value was 0.267 gram per kilo. per day. Some cases could be brought into nitrogen equilibrium on diets containing from 37 to 44 grams of protein, of which half was from animal sources, so long as the energy content was from 1.7 to 2.4 times the energy requirement.

CHEMICAL ABSTRACTS.

The Mode of Action of Narcotic Gases: Nitrous Oxide and Acetylene. HERMANN WIELAND (*Arch. expt. Path. Pharm.*, 1922, **92**, 96—152).—The vital activities of the round-worm, and the phase of muscular contraction which is independent of the

presence of oxygen, are no more affected by nitrous oxide or acetylene than by indifferent gases, whereas the higher animals are rapidly narcotised. From these experimental results, and from the similarity between the symptoms of nitrous oxide intoxication and of anoxæmia, it is argued that the narcotic effect of nitrous oxide and acetylene is due to an interference with the uptake or utilisation of oxygen by the nerve-cells. The fact that these two gases in particular exert a narcotic effect is ascribed to their relatively great solubility in water, which permits a high concentration to be attained in the blood. It is claimed that the experiments emphasise the distinction between the true lipid-soluble narcotics such as chloroform and the narcotic gases of the type of nitrous oxide.

C. R. H.

The Physiological Action of Metallic Ammines and Allied Compounds. AD. OSWALD (*Biochem. Z.*, 1922, 127, 156—167).—The action of a series of ammines of cobalt, nickel, and chromium and similar complexes of cobalt, iron, and chromium with ethylenediamine, pyridine, and phenanthroline and of complex oxalates and malonates has been studied on frogs, mice, and rats. A description of the physiological action of each is given, but in general the action of the ammines is that of ammonia or ammonia derivatives, that is initial stimulation of the motor centres followed by paralysis. The activity increases with the number of ammonia radicles. Unstable complex oxalates have the action of oxalic acid which is similar to that of the complex ammines, but the action of sodium chromomalonate has no similar action. The action of stable oxalates, for instance, potassium and rhodium oxalates, is therefore ascribed to their oxalate content and the action of ammines to their ammonia content.

H. K.

The Fate of Methyl and isoPropyl Alcohols in the Organism. JULIUS POHL (*Biochem. Z.*, 1922, 127, 66—71).—The normal urinary content of formic acid of dogs is increased many-fold by oral administration on successive days of 3 grams of methyl alcohol. Similar administration of isopropyl alcohol to dogs or rabbits leads to a combustion of about 88% in the body and an excretion of about 12%, chiefly in the form of acetone with a little isopropyl alcohol in the expired air.

H. K.

The Physiological Action of β -Amino-4-ethylglyoxaline (Histamine). PAUL SCHENCK (*Arch. expt. Path. Pharm.*, 1922, 92, 34—51).—Histamine is in general antagonistic to adrenaline (A., 1921, i, 640). Experiments on the surviving excised liver show, however, that histamine cannot antagonise the stimulating effect of adrenaline on the mobilisation of sugar; histamine itself, in fact, stimulates the latter process to some extent.

Anæmia could not be produced in guinea-pigs by prolonged administration of histamine.

C. R. H.

The Physiological Action of Melanin Acids. O. ADLER and W. WIECHOWSKI (*Arch. expt. Path. Pharm.*, 1922, 92, 22—33).—Intravenous injection of a 1% solution of the sodium salts of the

melanin acids, obtained by the oxidation of tyrosine with hydrogen peroxide and ferric chloride, or from cabbages, in doses of about 1 mg. per c.c. of blood, produces a state of incoagulability of the blood which lasts for several hours. Simultaneously, changes are observed in the form elements of the blood; in particular, there is a great reduction in the number of the blood-platelets after an injection.

C. R. H.

Physiology of the Phenols. II. Absorption, Conjugation, and Excretion. K. F. PELKAN and G. H. WHIPPLE (*J. Biol. Chem.*, 1922, 50, 499—511).—After intravenous injection in dogs, phenols rapidly disappear from the blood, being converted, in part, into conjugated phenols. On the other hand, ingestion in sufficiently large doses is followed by the appearance, for a short time, of free phenols in the blood and an increase in the content of conjugated phenols, the latter reaching a maximum in about an hour. The authors conclude from their results that toxic phenols (phenol and *p*-cresol) produced in the intestine from tyrosine by bacterial action are to a large extent oxidised in the organism, the remainder being conjugated in the liver with sulphuric or glycuronic acid and finally excreted in this form.

E. S.

[Fate of Tetrahydronaphthalene in the Organism.] W. RÖCKEMANN (*Arch. exp. Path. Pharm.*, 1922, 92, 52—67).—Tetrahydronaphthalene, a volatile constituent of floor-polishes, may be absorbed in appreciable quantities by inhalation.

As a result of feeding this substance to rabbits there was isolated from the urine an optically active (dextrorotatory) compound of the composition $C_{10}H_{12}O$; evidence is adduced to show that this is probably ac- β -tetrahydronaphthol; from the urine of dogs treated similarly, the only product obtained was dihydronaphthalene, and it is assumed that in this case the earlier metabolic product was ac- α -tetrahydronaphthol, which substance would lose water with great ease to give dihydronaphthalene.

C. R. H.

The Relative Toxicity of the Haloids and other Anions. A. T. CAMERON and M. S. HOLLENBERG (*J. Gen. Physiol.*, 1922, 4, 411—421).—Experiments were made on the survival times of frog's heart and muscle-nerve preparations in modified Locke solutions in which part or the whole of the sodium chloride had been replaced by equimolecular amounts of the sodium salt of other halogen acids or by sodium nitrate.

When more than 5% of the sodium chloride was replaced, the relative toxicities of the replacing ions were found to be as follows: $F' > IO_3' > I' > NO_3' > ClO_3' > Br' > Cl'$.

Relatively the greatest toxic effect was produced by the first slight replacement of the sodium chloride.

C. R. H.

The Toxicology of Arsine. II. Toxicity for Warm-blooded Animals. HERMANN FÜHNER (*Arch. exp. Path. Pharm.*, 1922, 92, 288—301).—A series of experiments with white mice shows that a minimum concentration in the atmosphere of 0.1 to 0.2 mg. of arsine per litre causes death from acute poisoning in

two to three hours. In these cases, post mortem estimations of arsenic show a concentration of 0.013 to 0.020 mg. of As_2O_3 per gram of body-weight. Death from delayed poisoning is induced by exposure for thirty minutes to a minimum concentration of from 0.1 to 0.15 mg. of arsine per litre, and the slowly poisoned animals show a concentration per gram of body-weight of 0.007 to 0.013 mg. of As_2O_3 .

The toxicity of arsine is not markedly greater than that of corresponding doses of sodium arsenite administered by subcutaneous injection.

C. R. H.

Toxicity of the Metallo-albumins. V. ARIOLA (*Arch. Farm. speriment. Sci. aff.*, 1921, **32**, 31—32, 33—39).—The metallo-albumins, obtained by shaking egg-albumin with powdered metals, exert a toxic action on *Colpoda cucullus* and vinegar eels, the intensity of the action with different metals diminishing in the order: cobalt, copper, iron, antimony, nickel, arsenic. Prolongation of the shaking at first enhances, but, if carried beyond a certain point, diminishes the effect of the resultant product.

T. H. P.

Toxicity of Metallic Powders. V. ARIOLA (*Arch. Farm. speriment. Sci. aff.*, 1921, **32**, 75—80, 88—90; cf. preceding abstract).—Powdered metals introduced under the skin of *Rana esculenta*, *Hyla arborea*, or *Bufo vulgaris* determine phenomena of paralysis, followed by death. In order of diminishing activity, the metals studied are arranged thus: antimony, copper, cobalt, and iron. Oxides of copper, cobalt, and iron also exhibit toxic effects, which are less than those of the corresponding metals.

T. H. P.

Pharmacological Action of Magnesium Sulphate and its Application in Strychnine Poisoning. MANFREDI FERRARA (*Arch. Farm. speriment. Sci. aff.*, 1921, **32**, 91—96, 97—98, 113—125).—Magnesium sulphate exerts a depressing action on the nervous system and when administered in large doses through the veins or spine produces complete paralysis and anaesthesia, often followed by death. The general effects produced by medium doses of the salt are of short duration. No true antagonism exists between the action of strychnine and that of magnesium sulphate, the latter exerting merely a retarding influence on the former.

T. H. P.

Chemistry of Vegetable Physiology and Agriculture.

Fat Metabolism of the Timothy Grass Bacillus. MARJORY STEPHENSON and MARGARET DAMPIER WHETHAM (*Proc. Roy. Soc.*, 1922, [B], **93**, 262—280).—Timothy grass bacillus was grown on a medium consisting of inorganic salts, including ammonia as the sole source of nitrogen, together with dextrose and sodium acetate. Estimations were made from time to time of the amounts of fat,

phosphatide, and protein, respectively. In each case a maximum is shown which almost coincides in time with the disappearance of dextrose and acetate from the medium. The organism is unable to utilise acetate in the absence of dextrose. Lactic acid (as lactate) gives results similar to those with dextrose. Both are utilisable alone. The acetic acid utilised in the presence of lactic acid or dextrose only affects the proportion of lipid material formed and does not increase the general growth. Propionic and butyric acids gave results similar to those with lactic acid. A method for estimating acetic acid is described. G. W. R.

The Production of Carbon Dioxide by the Typhoid Bacillus and the Mechanism of the Russell Double Sugar Tube. H. J. NICHOLS (*J. Infect. Dis.*, 1921, 29, 82—85).—The typhoid bacillus produces considerable amounts of carbon dioxide both from sugars and from proteins. The appearance of the Russell double sugar tube during the growth of the typhoid bacillus is not due to direct oxygen requirements, but (a) to the retention of carbon dioxide in the butt of the tube and its escape from the slant and (b) to alkaline reversion of other acids. CHEMICAL ABSTRACTS.

Rate of Formation and the Yield of Yeast in Wort. NORMAN A. CLARK (*J. Physical Chem.*, 1922, 26, 42—60).—A number of experiments on the rate of growth of yeast in beer wort, and in a sucrose medium are described together with experiments on the influence of alcohol, lack of bios, and crowding on the rate of growth. It is shown that if wort be seeded with "normal" actively budding yeast-cells (*Sacch. cerev.* race F.) and the culture is properly shaken and aerated at 25°, the rate of reproduction follows the logarithmic formula $\log C/C_0 = 0.160t$, from the moment of seeding until the crop reaches one hundred million cells per c.c., whether the seeding be five cells or eight million cells per c.c. or even more. At this point the solution contains 1.8 grams of alcohol per 100 c.c. When the concentration of alcohol exceeds 1.8% the constant k of the logarithmic formula must be replaced by a function of the percentage of alcohol, namely, $k = 0.2774 - 0.0806(\%) + 0.008543(\%)^2$, which holds from 1.8 to 5.0%. The crop of yeast reaches its maximum, about three hundred and twenty-five million cells per c.c., in about twenty-four hours; this maximum is independent of the seeding up to twenty-five million cells per c.c.; but if the wort be seeded up to four hundred million cells per c.c. the crop may reach six hundred and seventy-five million; this difference is to be ascribed to the lower content of alcohol. If wort be diluted with an artificial medium made up from sucrose and salts, the rate of reproduction is the same as in pure wort; the maximum crop is also the same, provided that the culture medium contains at least 10% of wort. In solutions containing less wort the rate is the same as usual, but the maximum crop is less; this must be ascribed to lack of bios in the culture liquid. Quantitative measurements of the maximum crop may be used as a convenient means of estimating bios. Washed yeast-cake rapidly absorbs bios from

wort, and if enough yeast is used the removal is practically complete and the cells do not bud. Under the experimental conditions, the rate of reproduction is independent of the concentration of sucrose and of bios; it is independent of the concentration of alcohol until this reaches 1.8 gram/100 c.c. The assumptions underlying Carlson's formula for the rate of reproduction of yeast are therefore without foundation (A., 1913, i, 117). J. F. S.

Action of Saponins on Yeast-cells. FRIEDRICH BOAS (*Ber. Deut. bot. Ges.*, 1922, 40, 32—38; cf. A., 1921, i, 294; A., 1922, i, 94).—The effect of different varieties of saponin on the alcoholic fermentation of sucrose by yeast was studied. Whilst with highly active saponins fermentation was inhibited owing to destruction of the yeast plasma, with less active saponins the rate of evolution of carbon dioxide was increased owing to increased permeability of the plasma membrane. The addition of salts generally inhibited fermentation. The action of different saponins on yeast may be correlated with their haemolytic activity. The action of saponin is due to its effect on the colloidal state of the lipid complex of the plasma membrane. G. W. R.

Decomposition of Lactic Acid by Yeast and by Blood-cells. OTTO FÜRTH and FRITZ LIEBEN (*Biochem. Z.*, 1922, 128, 144—168).—For the extraction of lactic acid the authors use and recommend Ohlsson's method (A., 1916, ii, 542), the removal of amyl alcohol by extraction with benzene being replaced by steam distillation. Yeast-cells and blood can destroy lactic acid, the most favourable condition in the case of yeast-cells being agitation of the medium in a brisk current of oxygen. Under such conditions 25—50 grams of press yeast destroy 0.2—0.3 gram of lactic acid in six to fourteen hours. The fate of the lactic acid is not known, but a portion appears as carbon dioxide. Yeast killed by acetone or heat cannot destroy lactic acid. H. K.

The Course of Alcoholic Fermentation in the Presence of Urea. MARTA SANDBERG (*Biochem. Z.*, 1922, 128, 76—79).—Top and bottom yeasts ferment sucrose in the presence of large quantities of urea with production of about 4% less alcohol than in the absence of urea. The urea is unchanged at the end of the fermentation. H. K.

Formaldehyde as an Intermediate Step between the Real Assimilation and the Formation of Carbohydrate in the Plant. II. MARTIN JACOBY (*Biochem. Z.*, 1922, 128, 119—121; cf. A., 1920, i, 800).—Leaves of *Tropaeolum majus* exposed to formaldehyde vapour show an increased weight of dry material which is independent of the presence of oxygen. H. K.

The Resorption of Aluminium Ions by the Roots of Plants. JULIUS STOKLASA [with J. ŠEBOR, F. TÝMICH, and J. CWACHA] (*Biochem. Z.*, 1922, 128, 35—47; cf. A., 1918, i, 475).—Hydrophytes, mesophytes, and xerophytes were grown in aqueous culture media

with and without addition of aluminium sulphate. Aluminium is absorbed by the first two groups, but only slightly by xerophytes, the roots taking up most. The amount absorbed falls off with increasing concentration of aluminium in the solution. Employing plants which absorb considerable amounts of aluminium, for instance, *Eriophorum vaginatum*, *Phragmites communis*, and *Carex riparia*, it was found that when aluminium or iron was absorbed, calcium, magnesium, and sodium appeared in the nutrient medium, and if both iron and aluminium were present together the absorption of either was partly inhibited and less of the other ions appeared.

H. K.

7 Behaviour of certain Organic Compounds in Plants. XIV.

G. CIAMICIAN and A. GALIZZI (*Gazzetta*, 1922, 52, i, 3—20).—The authors have investigated the resistance to oxidation by pulped spinach of uric and dimethyluric acids; aniline, acetanilide, and methylacetanilide; salicylic acid, methyl salicylate, and *m*-hydroxy-*p*-toluic acid; pyrrole- and dimethylpyrrole-carboxylic acids; phthalic and tetrahydrophthalic acids; aniline, α -naphthylamine, pyridine, and quinoline; carbamide and guanidine; eugenol, vanillin, and benzoic acid (cf. A., 1921, i, 483). The results obtained confirm the previous conclusion that the chemical actions of organic compounds on plants are not determined solely by etherification of the hydroxyl, amino-, and imino-groups, but are dependent also on other differences of constitution. The most poisonous products are not necessarily those most resistant to oxidation by vegetable enzymes.

Immersion of the leaves of *Prunus laurocerasus* in boiling water for some minutes results in the inactivation of the emulsin, whilst the oxidising enzymes present retain their activity. Amygdalin and saligenin are largely, and salicin completely, destroyed by the oxidising enzymes of pulped spinach. Thus, the oxidation of dextrose appears to catalyse that of the aromatic compound combined with the sugar. Tannin is far more resistant than pyrogallol to the oxidising enzymes of spinach.

It was previously found that, in general, fundamental compounds harmless to plants yield innocuous derivatives, but the fact that xanthine and ammonia were regarded as non-poisonous whereas theobromine, caffeine, and the amines are poisonous did not accord with this conclusion; further experiment shows that xanthine and ammonia exert a deleterious action on the bean plant.

The observation that esters are more injurious to bean plants than the corresponding potassium salts is confirmed by the results of tests with ethyl and potassium succinates and oxalates. The influence of alcohols is similar to that of the amines, as far as the development of the plants is concerned, although the phenomena characteristic of the alkaloids do not appear. Further, the action diminishes as the number of carbon atoms in the normal chain increases, with the exception that methyl alcohol, like methylamine, is the least harmful of the series. Like isoamylamine, isobutyl and isoamyl alcohols exhibit abnormally high toxicity, probably

owing to the presence of a methyl group in the side-chain of the alcohol radicle.

For compounds containing equal numbers of carbon atoms, the series: amines, alcohols, aldehydes, acids, represents the order of diminishing toxicity towards plants, the toxicity increasing with the resistance offered to enzymic oxidation. Acetone, methyl ethyl ketone, cyclohexanone, and 2-methylcyclohexanone appear to be without influence on bean plants. Experiments with glycolic and acetic acids, and with lactic and propionic acids, fail to reveal any specific influence of the substituted hydroxyl group. As regards the effect of a double linking, stearic and succinic acids are harmless to bean plants, whereas oleic, fumaric, and maleic acids retard development and cause darkening and ultimate drying of the leaves.

T. H. P.

The Chemical Composition of the Ergot of Diss and of the Ergot of Oats. GEORGES TANRET (*Compt. rend.*, 1922, 174, 827—830).—The ergot of diss, *Ampelodesmos tenax*, Linck, from North Africa, and the ergot of Algerian oats contain the same principles as the ergot of rye, but the proportions are very variable in passing from one species to another. The ergot of diss is poor in crystallised ergotinine, whilst that of oats, on the other hand, is richer than the average for the ergot of rye. The ergot of oats, but not the ergot of diss, could apparently be substituted for that of rye in years of scarcity.

W. G.

Proteins of the Adzuki Bean, *Phaseolus angularis*. D. BREESE JONES, A. J. FINKS, and C. E. F. GERSDORFF (*J. Biol. Chem.*, 1922, 51, 103—114).—The adzuki bean contains 21.13% of protein (N×6.25). By extraction with sodium chloride solution, an α - and a β -globulin were obtained which were separated by fractional precipitation with ammonium sulphate. Both globulins gave positive tests for tryptophan. They differed mainly in their sulphur content. Using Van Slyke's method, the following values were obtained for the diamino-acids: α -globulin—arginine 5.45, histidine 2.25, lysine 8.30, cystine 1.63; β -globulin—arginine 7.00, histidine 2.51, lysine 8.41, cystine 0.86%. The adzuki bean was also found to contain a small quantity of an albumin.

E. S.

The Carbohydrate Content of the Seed of *Asparagus officinalis*, L. W. E. CAKE and H. H. BARTLETT (*J. Biol. Chem.*, 1922, 51, 93—102).—The reserve carbohydrates of the asparagus seed consist of hemicelluloses. After removal of oil from the seed they may be extracted by dilute alkali, from which they are precipitated by acidification or addition of alcohol. Obtained in this way, the dry substance forms blue adsorption compounds with iodine which readily decompose on washing with water. Estimations of the carbohydrates in the seeds gave the following results: pentosans 2.02, galactans 0.42, dextrose 3.3, levulose 1.4, condensed mannose 21.8, condensed dextrose 15.1, condensed levulose 6.4%. From the values obtained for condensed sugar it is con-

cluded that the hemicelluloses occur either as mixtures of glucomannans and fructomannans or as glucofructomannans. Cellulose, starch, and inulin are absent from the seeds. E. S.

Nitrogen Distribution of Proteins extracted by 0.2 per Cent. Sodium Hydroxide Solution from Cotton-seed Meal, the Soja Bean, and the Coconut. W. G. FRIEDEMANN (*J. Biol. Chem.*, 1922, 51, 17—20).—The following results were obtained: Cotton-seed meal—amide-N 10.54, humin-N 2.09, cystine-N 1.11, arginine-N 23.48, histidine-N 4.94, lysine-N 5.10, amino-N of filtrate 51.26%. Soja bean—amide-N 11.31, humin-N 1.84, cystine-N 1.04, arginine-N 14.57, histidine-N 5.92, lysine-N 8.26, amino-N of filtrate 54.32%. Coconut—amide-N 7.40, humin-N 2.08, cystine-N 0.86, arginine-N 28.60, histidine-N 4.88, lysine-N 4.56, total-N of filtrate 51.35%. E. S.

The Rôle played by the Various Elements of the Wood of *Juniperus oxycedrus* in the Formation of Oil of Cade. R. HUËRRE (*J. Pharm. Chim.*, 1922, 25, 165—173, 214—221).—The various constituents of oil of cade are produced by the action of heat on certain well-defined constituents of the wood of *Juniperus oxycedrus*, of which two groups may be distinguished, namely, the water-soluble matter, the essential oil, a resin soluble in light petroleum and in ether, and a resin soluble only in ether, all of which contribute to the production of a pyrogenous oil lighter than water, and, secondly, a resin soluble in ethyl acetate, and the desinified wood itself, both of which furnish a tarry distillate heavier than water. The above elements of the wood give the following percentages of their weights of distillate: matter soluble in water 9%, essential oil 100%, resin soluble in light petroleum 55%, resin soluble in ether 45%, resin soluble in ethyl acetate 33%, wood 2%. The light oil obtained from the first group of materials acts as a solvent for the tar produced by the distillation of the entire wood, and if this is poor in essential oil, but little oil of cade is produced, whilst if it is also poor in resins soluble in ether and in light petroleum only a trace is obtained, consisting of tar heavier than water. G. F. M.

Volatile Oil of Milfoil. R. F. KREMERS (*J. Amer. Pharm. Assoc.*, 1921, 10, 252—261).—Dried *Achillea millefolium*, when distilled with steam, yielded 0.467% of oil, two specimens of which had respectively d_{20}^{25} 0.915, 0.913; acid number, 7.24, 4.27; ester number, 2.22, 5.65; saponification number, 9.44, 10.92; ester number after acetylation, 23.5, 17.8. The following substances were present: methyl alcohol, formaldehyde, ethyl alcohol, acetone, furfuraldehyde, valeric acid, formic acid, eugenol, pinene, nopinene, cineole, thujone, borneol, camphor, caryophyllene, and azulene.

CHEMICAL ABSTRACTS.

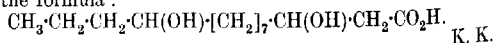
Spilanthal, the Pungent Principle of Para Cress. II. YASUHIKO ASAHINA and MICHIZÔ ASANO (*J. Pharm. Soc. Japan*, 1922, 85—97; cf. A., 1920, i, 654).—When hydrospilanthal is strongly pressed on a clay plate, its melting point is raised to

36—37° and its boiling point to 171°/6 mm. The analytical results correspond with the formula $C_{14}H_{29}ON$, and the acid obtained from it by hydrolysis (*loc. cit.*) gave an amide, m. p. 98°, and an anilide, m. p. 67—68°, which proved to be identical with decoamide and decoanilide. The authors next proceeded to synthesise the isobutylamides of decoic and *n*-nonoic acids. According to Fittig's method (*Annalen*, 1885, 227, 85), heptaldehyde was condensed with succinic acid, producing hexylparaconic acid, which when subjected to dry distillation yielded decenoic acid; this on reduction with hydrogen in the presence of platinum black gave decoic acid, m. p. 30—31°.

n-Nonoic acid was prepared by oxidising dihydroxystearic acid with chromic acid mixture. Decoisobutylamide, forms white needles, m. p. 37—38°, b. p. 171°/6 mm., and a mixture with hydrospilanthol melts at 36—37°. Nonoisobutylamide, forms white needles, m. p. 37—38°, b. p. 162°/6 mm., but a mixture with hydrospilanthol melts below 30°. It follows that hydrospilanthol is mainly composed of decoisobutylamide; the hay-like odour and bitter taste of the former depend on some impurities, which are not removed by mere distillation. K. K.

Constituents of the Seeds of *Pharbitis Nil Chois*. II. YASUHIKO ASAHINA and TORAJI SHIMIZU (*J. Pharm. Soc. Japan*, 1922, 1—18; cf. A., 1920, i, 360).—When pharbitin, a glucoside of the seeds, was hydrolysed with barium hydroxide, *d*- α -methylbutyric acid, b. p. 176°, d_4^{20} 0.9303, $[x]_D^{20} +19.33^\circ$, containing a small quantity of tiglic acid, was obtained. Niflic acid (*loc. cit.*) purified as its copper salt, $C_5H_8O_3Cu$, which forms blue crystals, was converted by distillation into tiglic acid and water, hence it is β -hydroxy- α -methylbutyric acid. In addition to pentose, rhamnose was isolated in crystalline form from the decomposition product of pharbitic acid. When ipurolic acid was warmed with hydriodic acid and red phosphorus in a sealed tube, a syrupy acid containing iodine was obtained, which gave myristic acid, m. p. 53.5°, when reduced with zinc and hydrochloric acid. The acid has therefore a normal carbon chain. When oxidised with nitric acid (*d* 1.35), ipurolic acid gave suberic and azelaic acids, whilst with hot chromic acid mixture, butyric acid and a diketone, white needles, m. p. 49° (*disemicarbazone*, aggregates of needles, m. p. 135°), were isolated in addition to the two acids above mentioned.

When ipurolic acid is boiled with acetic anhydride and sodium acetate, and the reaction product is saponified with alkali, an unsaturated monohydroxy-acid is produced, the reduction of which with hydrogen in the presence of platinum black gives a monohydroxymyristic acid, needles, m. p. 51°. When the acid is oxidised with chromic acid mixture, sebacic and butyric acids are obtained. From these results, the ipurolic acid is shown to be a β -hydroxy-acid of the formula:



K. K.

Pectinase produced by Different Species of *Rhizopus*. L. L. HARTER and J. L. WEIMER (*J. Agric. Research*, 1921, **22**, 371—377; cf. Harter and Weimer, *ibid.*, 1921, **21**, 609—625).—*Rhizopus* spp., parasitic on sweet potatoes, produce an enzyme which dissolves the middle lamellæ of the cells of the host plant. The relative activity of the pectinase produced was compared for nine parasitic and two non-parasitic species by noting the time required for maceration of disks of sweet potato. The results show considerable variation in the amount of mycelial enzyme and also in the amount excreted in culture solutions. Pectinase is produced even by the non-parasitic species. G. W. R.

The Efflorescences of *Rhodymenia palmata* ; Presence of a Xylan in the Floridean Algæ. C. SAUVAGEAU and G. DENIGÈS (*Compt. rend.*, 1922, **174**, 791—794).—The authors have obtained from the alga, *Rhodymenia palmata*, a pentosan which they have definitely identified as a xylan. It is admixed with a certain amount of a methylpentosan, which they were not able to identify. They were not able to find any indication of the presence of either mannitol or trehalose. W. G.

Velocity of Reaction of Vegetable Enzymes. I. Influence of the Concentration of the Enzymes on the Velocity of Action of the Enzymes of Germinated Barley. DARIO MAESTRINI (*Arch. Farm. speriment. Sci. aff.*, 1921, **32**, 40—48, 49—59).—Measurements of the velocities of action of the three principal enzymes of germinated barley, namely, amylase, protease, and lipase, yield results in contradiction with the law of Schütz and Borissow, which states that the velocity of peptic digestion is proportional to the square root of the amount of the enzyme. The amylolytic and proteolytic actions of extract of germinated barley may be completely inhibited by addition of dextrose and peptone respectively. During the final period of the enzyme action, the amount of hydrolytic products produced is greater with the smaller concentrations of the enzyme; this result appears to depend on accumulation of the products of the action, since removal of these results, in the case of amylase, in renewal of the hydrolysis. T. H. P.

Velocity of Reaction of Vegetable Enzymes. II. Effect of Hydrogen Ions and of Salts on the Velocity of Action of the Enzymes of Germinated Barley. DARIO MAESTRINI (*Arch. Farm. speriment. Sci. aff.*, 1921, **32**, 99—112; cf. A., 1920, i, 273, 413; 1921, i, 152, 281, 628).—Treatment of germinated barley with 0.3% acetic acid solution having electrical conductivity $\lambda = 14 \times 10^{-4}$ yields an extract having very high amylolytic activity. As the concentration of the acid is increased, the activity diminishes until it becomes almost zero for 0.9% acid, having $\lambda = 45 \times 10^{-4}$. With proteases (lipases), the optimum activity is obtained with about 0.4% acetic acid solution, having $\lambda = 28(26) \times 10^{-4}$; 0.9% acid gives an extract of very low proteolytic and lipolytic activities. The enzymic activity of these extracts appears to be proportional, within certain limits, to the concentration of the hydrogen-ions.

The author's results with malt amylase furnish no support for Duclaux's statement that calcium chloride inhibits completely the action of vegetable enzymes. The activity of malt diastase may be enhanced by chlorides, such as those of sodium and calcium, provided that the hydrogen-ion concentration of the enzyme solution is not at its optimum value. Cadmium chloride inhibits the amylolytic action of germinated barley extracts. T. H. P.

Velocity of Reaction of Vegetable Enzymes. III. Effect of the Quantity and Volume of the Substrate on the Activity of the Amylase of Germinated Barley. DARIO MAFSTRINI (*Arch. Farm. speriment. Sci. aff.*, 1921, **32**, 126—128, 129—133).—The results of the experiments here described show that, as regards the absolute quantity of the substrate, the behaviour of malt amylase closely resembles that of ptyalin (cf. Bielfeld, A., 1901, ii, 561) and that of emulsin, the quantity of reducing sugars produced being directly proportional to the absolute quantity of substrate used. Increase in the amount of the latter without increase of its concentration does not greatly affect the production of reducing sugars by amylase under the experimental conditions employed. Gradual increase of the volume of the substrate by addition of water is accompanied by a corresponding diminution in the activity of the amylase. T. H. P.

Analysis and Composition of Maize Pollen. R. J. ANDERSON and W. L. KULP (*J. Biol. Chem.*, 1922, **50**, 433—453).—Pollen from three different varieties of maize was investigated. Considerable variations in composition, especially as regards starch and sucrose, were found, but it is possible that these were due to differences in the degree of ripeness. From the ripe pollen of the variety mainly examined were isolated: choline, *l*-proline, inositol, a substance melting at 88—89° which was probably myricyl alcohol, and an amorphous and a crystalline phosphatide. The amorphous phosphatide gave on hydrolysis choline and a small quantity of another base which formed an aurichloride containing Au 49.84% and having m. p. 132°, glycerophosphoric acid, a saturated fatty acid, m. p. 63°, which was probably palmitic acid, and a small quantity of an unidentified unsaturated fatty acid. It was also found to contain sulphur. The crystalline phosphatide was hygroscopic after drying over sulphuric acid, and contained nearly two atomic proportions of nitrogen to one of phosphorus. E. S.

Absorbent Power of Soils, and the Absorption by Plants of Nutritive Substances from the Soil. LUIGI CASALE (*Staz. sper. agr. ital.*, 1921, **54**, 65—113).—The causes determining the absorbent power of soils are the same as those which govern absorption by colloids. The colloidal constituents of the soil acquire a positive or negative charge by yielding anions or cations to the liquids moistening them; the positive colloids are considered to be absorbed by the mass of the negative colloids, and the absorption of cations to take place as soon as the necessary difference of

potential is established between a colloid particle and the zone of concentration of kations round it. The coagulating power of various electrolytes is given by the decreasing order: $\text{Fe} > \text{Al} > \text{Mg} > \text{Ca} > \text{K} > \text{NH}_4 > \text{Na}$; in general, the coagulating power of the electrolyte is the greater the lower the solution tension of the kation and the greater its relative velocity, sodium being an exception. The anion of electrolytes also influences the coagulating power. Absorption by colloids is exerted on the entire zone of concentration. From the complex solutions which moisten the soil, potassium and ammonium ions are more absorbed than those of calcium, magnesium, and sodium. The last to be absorbed form the outermost layers, and being most easily redissolved, are most easily replaced by other bases; the substitution is therefore not chemical, but electrical in character. In order that absorption can occur, the colloid must acquire a negative charge by sending positive ions into solution. Basic silicates and humates, after being treated with boiling hydrochloric acid and washed, cannot do so, and therefore lose their absorbent power. The behaviour of organic colloids is exactly identical with that of inorganic colloids treated with metallic salts of solution tension lower than that of hydrogen. The ectoplasm of the absorbent cells of a plant sends hydrogen-ions into solution and thus acquires a negative charge which is less than that of the colloids of the soil, so that there is a difference of potential between the plant and the soil; the colloidal particles are consequently attracted and adhere to the absorbent zone, and, in endeavouring to equalise their negative charge with that of the ectoplasm, send kations towards it, establishing a kind of continuity. Equalisation does not, however, occur, since the absorbed ions are attracted by the tonoplast in an identical manner; they thus pass through the protoplasmic mass and can be utilised. The passage of nutritive substance from cell to cell is governed by the same causes as those controlling absorption. The beneficial action of fertilisers is explained by the action which their kation has in lowering the negative charge of the colloids, thus raising the difference of potential between them and the plant.

CHEMICAL ABSTRACTS.

Factors affecting the Hydrogen-ion Concentration of the Soil and its Relation to Plant Distribution. W. R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1922, **16**, 369—413).—A comprehensive survey is given of modern theories on soil reaction. The buffer system in soils is discussed. Whilst the maximum alkalinity due to calcium carbonate in the soil is P_{H} 9.01, in the presence of carbon dioxide lower alkalinities are obtained owing to the formation of calcium hydrogen carbonate. In the presence of magnesium carbonate, alkalinity up to P_{H} 10.0 is possible, a circumstance which may explain the supposed unfavourable effect of lime prepared from dolomitic limestone. Alkalinities of more than P_{H} 10.0 are possible where sodium carbonate is present in the soil. In such cases, the alkalinity may be reduced to P_{H} 8 by additions of calcium sulphate. A survey of soils derived from different rocks

shows the influence of geology on soil reaction. This relation is also modified by topographical factors. Records are given for the soil reaction of the habitats of a large number of native plants. Data are also given for the reaction of spring- and river-waters.

G. W. R.

Relation of the Hydrogen-ion Concentration of the Soil to Plant Distribution. E. A. FISHER (*Nature*, 1921, 108, 306; cf. Atkins, this vol., i, 415, and preceding abstract).—The apparent p_H of the soil, as determined colorimetrically, is often influenced by the fineness of division of the sample. Moreover, the actual p_H of the soil at the moment of measurement is sometimes of less importance than the rate of change of the p_H under natural conditions. The buffer effects imposed by the nature of the soil on its reaction vary enormously in magnitude with different soils. It is suggested that measurements should be made, not merely of the p_H of soils, but also of the variations in p_H with addition of acids and alkalis; the titration curves could then be correlated with the magnitude of the buffer action of the soil.

A. A. E.

Factors in the Development of Soil Acidity. J. KÖNIG, J. HASENBÄUMER, and E. KRÖGER (*Z. Pflanz. Düng.*, 1922, [4], 1, 3—12).—Estimations of the P_H of soil moisture were made in order to determine the effect of different soil dressings, the effect of the growth of individual species of plants with varying manurial treatment, and the effect of different species of plants on soil acidity. The experiments were carried out in zinc pots. Even without the addition of any dressing, there was a slight increase in acidity after eight months, probably owing to defective aeration. Slight increases of acidity were observed as the result of normal applications of superphosphate, potassium salts, and ammonium salts. Sodium nitrate, "nitrolimc," and basic slag had little effect, whilst calcium carbonate decreased the soil acidity. Similar results were obtained when the soil carried a crop of oats. In the experiments with different crops, peas, lupines, and buckwheat produced a slight increase in acidity, whilst maize, grass, clover, and mustard gave slight decreases. These results are in agreement with observations on the acidities of the root sap of the plants used.

G. W. R.

Soil Acidity and its Effect on Germinating Plants. OTTO LEMMERMANN and L. FRESSENIUS (*Z. Pflanz. Düng.*, 1922, [4], 1, 12—32; cf. A., 1921, ii, 516).—Three types of soil acidity may be distinguished, namely, the actual acidity of the soil moisture due to the presence of acids, the latent acidity developed in the presence of solutions of neutral salts due to base exchange whereby salts of iron and aluminium appear in the soil extract and produce acidity by hydrolysis, and the latent acidity developed in the presence of salts of weak acids and strong bases where the base is absorbed by the soil colloids and the acid remains in the extract. The greatest acidity is found in the latter case and is not considered as of importance from a plant physiological point of view. The

three types of acidity for a number of soils as measured by the titratable acidity and by the P_H were compared. Whilst the results show a general agreement, the order of acidity is not quite consistent between the three series. Experiments with seedlings grown in sand cultures with the addition of varying amounts of sulphuric acid in the water supplied show that cereals have differing toleration. Oats showed the greatest toleration of acidity, whilst wheat was the most sensitive. In the case of oats, a concentration of 0.05% of sulphuric acid was required to produce injury. The effect on the titratable latent acidity of the soil extract of the previous addition of varying amounts of sulphuric acid is shown by curves giving the relation between the amount of sulphuric acid added and the titratable latent acidity of the soil extract. The curves for soils treated with sodium acetate show higher acidities than in the case of soils treated with potassium chloride. In the case of the potassium chloride series, the amount of sulphuric acid required to produce a titratable acidity in the extract sufficient to cause injury (as shown by the sand culture experiments) gives an expression for the amount of added acid which will produce harmful effects on plant growth. Results obtained with sodium acetate and similar salts are not regarded as trustworthy criteria as to the acidity of the soil for plant physiological purposes. From the differing tolerations of plants to acidity, the acceptance of any particular degree of acidity, measured as P_H , as critical is not to be recommended. Soil acidity must be considered in relation with the manurial treatment. Soils may have little active acidity, but marked latent acidity. With such soils no injurious effect due to acidity is observable unless dressings of salts such as potassium chloride are given.

G. W. R.

Displacement Method for Obtaining Soil Solution. F. W. PARKER (*Science*, 1921, 54, 438—439).—The method, which is essentially that of Itscherekov (*J. expt. Landw. [Russia]*, 1907, 8), consists in displacing the soil solution from soil packed in brass or glass cylinders, by means of ethyl alcohol. The latter, as it percolates through the soil, displaces some of the soil solution which forms a zone of saturation below the alcohol; this zone increases in depth as it is continually forced downwards by the alcohol, and is ultimately delivered free from alcohol. From 35 to 75% of the soil solution may be obtained by this method. Successive portions of the displaced solution have the same composition, and the results indicate that the true soil solution is secured.

A. A. E.

Basic Exchange in Soils. VON NOSTITZ (*Mitt. deut. landw. Ges.*, 1921, 36, 608—610).—A review of the present state of knowledge regarding absorption and basic exchange in soils, with particular reference to the work of Ramann (A., 1917, ii, 468; 1919, i, 615; ii, 154; 1920, ii, 257), which is of importance inasmuch as permutite-like hydrated aluminium silicates are fairly widely distributed in soils. The author has shown that even crystalline silicates such as mica and feldspar can to a certain extent exchange

their potash for other bases; thus excessive liming may cause potash impoverishment. Certain soils can be deprived of all basic elements by repeated treatment with ammonium nitrate; after treatment of such a soil with a solution containing ammonium, calcium, and magnesium salts, plants die soon after germination with typical symptoms of potash-hunger, whereas appropriate addition of potassium salts restores the fertility.

CHEMICAL ABSTRACTS.

The Nature of certain Aluminium Salts in the Soil and their Influence on Ammonification and Nitrification. IRVING A. DENISON (*Soil Science*, 1922, **13**, 81—106).—By the analysis of dialysed extracts from some acid soils, it is shown that the soluble aluminium in soils is not in the form of salts but of colloidal aluminium hydroxide. Increased hydrogen-ion concentration brought about by the formation of mineral acids, by adsorption of basic ions from salts, may ultimately produce soluble aluminium salts. The presence of soluble aluminium salts is the result rather than the cause of soil acidity. Ammonification is stimulated by aluminium salts, but nitrification suffers a temporary check. Calcium carbonate is the most effective agent for the removal of soluble aluminium salts from soils. A. G. P.

Substances Dissolved in Rain and Snow. SHERMAN SCHAFFER (*Chem. News*, 1922, **124**, 35—36).—Forty-five samples of rain and snow which fell between August 18th, 1920, and June 1st, 1921, have been analysed. The deposits consisted of 18·14 in. of rain and 34·0 in. of snow, which fell in Mount Vernon, Iowa. During the period 0·60126 lb. of nitrates, 0·03985 lb. of nitrites, 1·48045 lb. of free ammonia, 1·16022 lb. of albuminoid ammonia, 34·43179 lb. of chlorides, and 102·08035 lb. of sulphates calculated as SO_3 , fell per acre. Generally, the author finds no seasonal change in the amount of these substances deposited. The nitrates had an average value of 0·3 per million of rain with a maximum of 1·0 per million, the average for the nitrites was 0·0033 per million with a maximum of 0·03 per million; free ammonia had an average of 0·67 and a maximum of 2·1 per million, whilst the average for albuminoid ammonia was 0·38 and the maximum 2·0 per million. The chlorides had an average of 10·1 and a maximum of 49·7 per million. It is shown, from an analysis of the sodium and potassium in the chloride, that these do not come from ocean spray, but probably from coal smoke. The average for the sulphates was 29·9 and the maximum 101·2 per million. Sulphites were also estimated, seven samples showed no sulphite, whilst the remaining samples had an average of 1·43 parts per million with a maximum of 1·8 per million. The total nitrogen which fell in this period was 3·28178 lb. per acre and consisted of 5·74% nitric acid, 0·51% nitrous acid, and 93·73% ammonia. J. F. S.

Organic Chemistry.

Natural System of Carbon Compounds. II. Empirical and Rational Allologous Series and their Graphical Representation as a System. HERMAN DECKER (*Helv. Chim. Acta*, 1922, 5, 285—299; cf. this vol., i, 417).—Series of compounds are termed allologous when the formulæ of members conform to a general expression. The special type of allology in which the formulæ of compounds differ by $(\text{CH}_2)_n$, is termed empirical homology. These definitions, however, permit the inclusion in one class of structurally different compounds. Rational homology, exhibited by compounds the interconversion of which may be conceived by addition or removal of $\cdot\text{CH}_2\cdot$ groups, may be direct or indirect, according as the relationship is analogous to that of direct descent or of cousinship in human genealogy. Irrational homology, exemplified by the acetylenes and the allylenes, is specially frequent among aromatic compounds. Among hydrocarbons, C_nH_m , the following types of rational allology (of which the respective series equations are indicated) are at present distinguishable:—*homologues*—paraffins ($n-m/2+1=0$), ethylenes ($n-m/2=0$), acetylenes ($n-m/2-1=0$), benzene homologues ($n-m/2-3=0$), naphthalene homologues ($n-m/2-6=0$); *centrologues*—acetylene, benzene, . . . ($n-m=0$); *phenylogues*—benzene, diphenyl, . . . ($n-3/2m+3=0$), toluene, diphenylmethane, . . . ($n-3/2m+5=0$), ethylbenzene, diphenylethane, . . . ($n-3/2m+7=0$); *benzologues*—benzene, naphthalene, . . . ($n-2m+6=0$), diphenyl, phenylnaphthalene, . . . ($n-2m+8=0$), pyrene, isoperilene, . . . ($n-2m+4=0$); and *perilogues*—naphthalene, pyrene, . . . ($n-3m+14=0$); anthracene, perilene, . . . ($n-3m+16=0$). The series equations show that each of these may be represented by straight lines, of which the angle of inclination to the n -axis is termed the specific constant of the type. The discussion of the results of this mode of representation does not lend itself to abstraction. J. K.

Some Compounds of Bivalent Carbon. ALFRED GILLET (*Bull. Soc. chim. Belg.*, 1922, 31, 126—131; cf. this vol., i, 213).—A development of the theory put forward in the previous paper. Various data are tabulated and the conclusion is drawn that, of all the known saturated isomerides, the compound which is most closely related in formula to the corresponding unsaturated compound differs least in boiling point from the latter. Some connexion between these differences and their variations in various series of compounds is deduced. H. J. E.

Oxidation of Aliphatic Hydrocarbons with Nitrogen Peroxide. II. CH. GRÄNACHER and P. SCHAUFELBERGER (*Helv. Chim. Acta*, 1922, 5, 392—395; cf. A., 1921, i, 2).—Neither palmitic nor stearic acid could be detected among the acids obtained by the oxidation of paraffin (m. p. 50—52°) with nitrogen peroxide VOL. CXXII. i.

(cf. Bergmann, A., 1918, i, 285). The main fraction, b. p. 240–300°/23 mm., of the esterification product of the acid mixture furnished an *ester*, leaflets, m. p. 40·5°, from which a saturated *acid*, $C_{22}H_{44}O_2$, leaflets, m. p. 59–60°, was obtained. Since these are not the properties of behenic acid, the new acid must contain a branched chain structure, and it is concluded that paraffin contains considerable quantities of hydrocarbons, other than normal. From a fraction, b. p. 90–135°/12 mm., of the esterified product, a *lithium salt*, $C_{14}H_{27}O_2Li$, was obtained, corresponding with a saturated liquid hydroxy-acid, probably naphthenic acid or containing a branched chain structure. Another fraction, b. p. 135–155°/12 mm., similarly furnished a *lithium salt*, $C_{15}H_{29}O_2Li$, also derived from an analogous hydroxy-acid. J. K.

Preparation of Fatty Acids, Aldehydes, and Ketones from Mineral and Tar Oils. CARL HARRIES (D.R.-P. 339562; from *Chem. Zentr.*, 1921, iv, 1222).—The raw oils before oxidation with ozone are treated with liquid sulphur dioxide to remove the portions soluble therein. For example, the tar from bituminous coal is treated with liquid sulphur dioxide, whereby strongly unsaturated compounds are removed, less unsaturated compounds with double linkings remaining behind in the residue. This is cooled to the point of partial solidification and the portion remaining liquid, the so-called "Schwitz" oil, is run off and fractionated with steam. The fraction between 100 and 250°/10 mm. is treated with ozone until the increase in weight amounts to 8–12%. The oxidised oil is then treated with superheated steam to decompose the peroxides formed and the acids are separated from the unattacked portion by hot concentrated potassium hydroxide. The resultant soaps are separated from the oil by treatment with superheated steam. The soaps thus obtained on hydrolysis give principally palmitic and stearic acids. The material after the removal of the soaps still contains unsaturated compounds and the portion containing aldehydes is again treated with ozone, steam, and potassium hydroxide, whereby aldehydes are converted into acids. The yield of fatty acids, for the most part crystalline, amounts to about 18–20% of the Schwitz oil. In order to obtain aldehydes and ketones, the ozonised material after treatment with steam is shaken with sodium hydrogen sulphite and the aldehydes and ketones are recovered by way of the bisulphite compounds. A large number of aldehydes and ketones are obtained boiling over a large range. A yield of aldehydes and ketones up to 80% may be obtained if the ozonides are treated with sodium hydrogen sulphite or potassium ferrocyanide in the presence of potassium hydrogen sulphate. The residual "Schwitz" oil after treatment with sulphuric acid is no longer oxidisable and has m. p. –6° to 1°, according to origin; b. p. 280–350°/760 mm. G. W. R.

Preparation of Diolefines and Polymerisation Products Thereof. H. OTTO TRAUN'S FORSCHUNGLABORATORIUM (Brit. Pat. 156116).—Diolefines are obtained by heating together for a suitable

time under pressure at a sufficiently high temperature molecular quantities of acetylene and ethylene hydrocarbons in presence or absence of a catalyst, for example, anhydrous alkali hydroxides, and if either the pressure or temperature or time of interaction be increased polymerisation products of the diolefines are obtained in a single operation. For example, a mixture of acetylene and propylene in approximately molecular proportions is forced into a thick-walled spiral or autoclave at 3–15 atmos. pressure and heated at 350–450°. The spiral is provided with a non-return inlet valve and an outlet valve which can be regulated to release the gases at any desired pressure. The escaping gases are cooled and the diolefine condenses, unchanged gas being recirculated through the apparatus. By using an indifferent gas as a diluent to increase the pressure to, say, 30 atmos. the yield of diolefine, in the present instance isoprene, can be increased to 85% of the theoretical. When the operation is performed in an autoclave and the heating is continued for ten to fifteen hours at 55–65 atmos. pressure the diolefine undergoes polymerisation to rubber-like substances together with intermediate products which can be utilised as varnish and turpentine substitutes.

G. F. M.

Preparation of Diolefines and Derivatives Thereof. H. OTTO TRAUN'S FORSCHUNGS-LABORATORIUM (Brit. Pat. 156122).—Halogenated derivatives of diolefines are obtained by the pyrogenetic decomposition of hydrocarbons such as turpentine, dipentene, or limonene in presence of halogens or hydrogen haloids, the reactions being accelerated by catalysts such as silicon alloys, silicates, or metallic platinum. Similar diolefine derivatives are also produced by the chlorination of pentane or isopentane at 600–800°. From these stable derivatives the unstable diolefines may readily be obtained as required for use by splitting off hydrogen haloid. By way of example, a mixture of equal volumes of benzene and limonene vapours and hydrogen chloride is passed through a ferro-silicon tube heated at 550–600°, or, alternatively, a mixture of 1 vol. of gasolene vapour (b. p. 40–45°) and 4 vols. of chlorine is similarly treated at 600–800°, and the chlorinated products, consisting mainly of dichloropentanes, are led into a suitable water-cooled condenser and collected. The yield of compounds from which diolefines suitable for caoutchouc synthesis can be obtained amounts to 60–80% of the theoretical.

G. F. M.

Compounds of Acetylene with Silver Phosphate and Silver Arsenate. P. BENEDICT OBERDOERFER and J. A. NIEUWLAND (*J. Amer. Chem. Soc.*, 1922, **44**, 837–840).—The formula assigned to their acetylene silver phosphate compound by Nieuwland and Maguire (A., 1906, ii, 721) is now shown to be incorrect. The substance which they analysed contained small amounts of water and free phosphoric acid. Analytical results from the carefully purified substance give the following formula to the compound, $6(\text{Ag} \cdot \text{C} \equiv \text{CH})_2 \cdot \text{Ag}_2\text{HPO}_4$.

An acetylene silver arsenate has also been prepared by the same

method, and the analytical data point to the constitution $2(\text{H}_3\text{AsO}_4)\cdot\text{Ag}_3\text{AsO}_4\cdot 4\text{C}_2\text{Ag}_2$. Its properties are similar to those of acetylene silver phosphate (*loc. cit.*).

W. G.

The Interaction of Methyl Iodide and Potassium Plumbite. J. G. F. DRUCE (*Chem. News*, 1922, **124**, 215—217; cf. A., 1920, i, 426).—Contrary to the behaviour of alkaline solutions of stannous hydroxide, it is shown that no organo-metallic compounds are obtained with potassium plumbite and methyl iodide. The constitutional formulæ of the potassium hydrogen plumbites and stannites are discussed.

W. E. C.

Preparation of Vinyl Compounds and Polymerisation Products Thereof. H. OTTO TRAUN'S FORSCHUNGS-LABORATORIUM (Brit. Pat. 156117).—The addition of hydrogen haloids, methyl haloids, or organic carboxylic acids to acetylene hydrocarbons takes place smoothly and rapidly at 100—120° under a pressure of 1—2 atmos. By increasing the pressure and by raising the temperature when all the acetylene is absorbed, polymerisation products of the vinyl esters are obtained without the necessity of isolating the intermediate product. Although the reactions proceed quite satisfactorily without catalysts, they can be accelerated if desired by the addition of small amounts of certain metals or metallic compounds (other than mercury compounds, the use of which is already known, and involves troublesome regeneration processes) such as magnesium, tin, or copper, or their compounds, iodine, hydriodic acid, boron compounds, or organic acid anhydrides. If the acetylene is diluted with an inert gas such as nitrogen, or with benzene or petroleum vapour, the pressures can be increased to 10—15 atmos. or more and the reaction correspondingly accelerated without risk of explosion of the acetylene. Examples: (1) 40 parts of allylene and 36—38 parts of dry hydrogen chloride are heated at 120° at 1—2 atmos. pressure for ten to twenty-four hours. Yields of 80—85% of β -chloropropylene and 10—15% of another chloro-compound are formed, and the former can be completely polymerised by further heating at 150—200°. The polymerisation is accelerated by increasing the pressure to, say, 15 atmos. by the introduction of nitrogen. The polymerisation product can be employed for the preparation of varnishes, or can be transformed into rubber-like substances by the removal of the halogen by the action, for example, of sodium, calcium, or magnesium in presence of an inert organic liquid. (2) Twenty-six to twenty-eight parts of acetylene are gradually introduced into a mixture of 50 parts of acetic acid and 1 part of acetic anhydride. The mixture is heated at 40—60° and the pressure raised to 5 atmos. by the introduction of nitrogen. The product consists of 75 parts of vinyl acetate and 3—5 parts of ethylidene diacetate. If the temperature is then increased to 120—200° and the pressure to 10 atmos. or more, the esters are polymerised to products which vary in consistence from semi-liquids to more or less tough solids, according to the extent to which the polymerisation is allowed to proceed.

G. F. M.

Preparation of Vinyl Haloids. H. OTTO TRAUN'S FORSCHUNGS-LABORATORIUM (Brit. Pat. 156120).—Vinyl haloids are obtained in good yield without the intermediate isolation and purification of acetylene by the action of concentrated aqueous hydrogen haloids at 60–95° on calcium carbide in the presence of a catalyst, preferably a mixture of a mercury and a copper salt. The reaction occurs without catalysts if the pressure is increased above atmospheric, but some of the vinyl haloid is polymerised under these conditions. The vinyl chloride distils off as it is formed, and if a stream of hydrogen chloride is passed through the reaction mixture during the operation the yield is almost quantitative. Small quantities of zinc, aluminium, or tin chlorides accelerate the addition of hydrogen chloride to the nascent acetylene, but ferric chloride accelerates the reaction in the direction of the formation of dichloroacetaldehyde. G. F. M.

The Labile Nature of the Halogen Atom in Organic Compounds. II. Action of Hydrazine on Nitrogen-Halogen Compounds and on Bromomalononic Esters. EDMUND LANGLEY HIRST and ALEXANDER KILLEN MACBETH (T., 1922, 121, 904–511).

The Labile Nature of the Halogen Atom in Organic Compounds. I. Titanium Reductions of Substituted Nitro-paraffins. THOMAS HENDERSON and ALEXANDER KILLEN MACBETH (T., 1922, 121, 892–903).

The Surface Tension of Mixtures of Alcohol and Water at 25°. LOUIS LEIGHTON BIRCUMSHAW (T., 1922, 121, 887–891).

Co-ordination Forms of Glycerides. I. KLINMONT (*Oesterr. Chem. Ztg.*, 1922, 25, 63–64).—A reply to Grün (this vol. i, 420). H. W.

Properties of Mixtures of Ethyl Ether, Sulphuric Acid, and Water. JAMES ROBERT POUND (T., 1922, 121, 941–945).

Preparation of Alkyl Sulphates. HENRY DREYFUS (Brit. Pat. 177189).—Ethyl sulphate or its homologues are obtained by heating alkali pyrosulphates (2 mols.) or chlorosulphonates (2 mols.) with ethyl alcohol or ethyl ether or their homologues (2 mols.) and after four to five hours, distilling off the ester, preferably in a vacuum. Alternatively, the alcohol vapours may be passed over sodium pyrosulphate heated at 150° in a vacuum, whereby ethyl sulphate together with unchanged alcohol distils off as fast as it is formed. G. F. M.

Preparation of Vinyl Sulphuric Acid and Homologues thereof. H. OTTO TRAUN'S FORSCHUNGS-LABORATORIUM (Brit. Pat. 156121).—Vinyl sulphuric acid is formed almost quantitatively according to the equation $\text{CH}_2\text{CH} + \text{H}_2\text{SO}_4 = \text{CH}_2\text{CH}\cdot\text{SO}_3\cdot\text{OH}$, when cold anhydrous sulphuric acid (96 parts) is gradually saturated, at temperatures below 0°, with 26 to 28 parts of acetylene at

2 to 5 atmos. pressure, preferably in presence of small quantities of a catalyst such as mercuric sulphate. Homologues of acetylene can be used in a similar way.

G. F. M.

Trimethylene Dinitrate. F. BLECHTA (*Z. ges. Schiess-Sprengstoffw.*, 1922, 17, 57—58).—Pure trimethylene glycol (b. p. 211—212°/741 mm., d_{15}^{20} 1.054) was nitrated in Schlögel's apparatus, the composition of the mixed acids being nitric, 25.26%, sulphuric, 66.55%, water, 8.19%. Ten grams of the glycol were slowly dropped into 200 grams of mixed acids cooled to 8° with violent agitation. The increase of temperature was much greater than in the nitration of glycerol, and drops hanging from the funnel on being splashed with the acids ignited regularly. The nitrate obtained was washed with cold water, 2% sodium carbonate solution, and finally several times with cold water and dried to constant weight in a vacuum over sulphuric acid. The nitrogen content was 16.7% (theoretical, 16.87%). The product was similar to glyceryl nitrate but less viscous; d_{15}^{20} 1.408. It was miscible in all proportions with methyl alcohol, ether, chloroform, benzene, or acetone, only slightly soluble in carbon bisulphide, solubility in 96% ethyl alcohol 1:5, solubility in water at 26° 1:410. No signs of crystallisation occurred on cooling for three hours at -20°. Tested by Abel's method at 83°, it showed slightly less stability than glyceryl nitrate. Its sensitiveness to impact is the same as that of the latter.

H. C. R.

Symmetrical Dibromopivalic Acid and 1-Methylcyclopropane-1-carboxylic acid. MORITZ KOHN and ANISSIM MENDELEWITSCH (*Monatsh.*, 1921, 42, 227—244).—Symmetrical dibromopivalic acid and from it dihydroxypivalic acid were synthesised by the following steps. Two mols. of formaldehyde and 1 mol. of propaldehyde were condensed in aqueous potassium hydroxide to dihydroxy-*xx*-dimethylpropaldehyde, which was converted into its oxime. The oxime, which readily decomposes on heating, was boiled with excess of acetic anhydride whereby it was converted into diacetoxypivalonitrile. By heating in a sealed tube at 125—130° for twenty hours with saturated hydrobromic acid, the nitrile was converted into *dibromopivalic acid*, $\text{CMe}(\text{CH}_2\text{Br})_2\text{CO}_2\text{H}$, m. p. 56—58°, crystallising from light petroleum in rhombic pyramids [$a:b:c=0.8949:1:0.7789$], d 2.078. By boiling with lead oxide and water, the dibromopivalic acid was converted into *dihydroxypivalic acid*, m. p. 179—182°, crystallising from water in small, acute rhombohedra or tetrahedra belonging to the trigonal-pyramidal class of the rhombohedral system. [$a:c=1:1.2549$], d 1.329. The product obtained by Koch and Zerner (*A.*, 1901, i, 633), m. p. 163—164°, was evidently impure.

Methyl dibromopivalate has b. p. 229—231°. *Methyl dihydroxypivalate* was prepared by alkylating dihydroxypivalic acid with diazomethane. It forms apparently rhombic, very deliquescent prisms, m. p. 40—45°, b. p. 145°/20—22 mm.

By reduction of the methyl ester of dibromopivalic acid in methyl alcohol with zinc dust, *methyl 1-methylcyclopropane-1-carboxylate*

was formed; it is a colourless, mobile liquid, b. p. 121—123°, with a camphor-like odour. The free acid crystallises from water in spear-shaped crystals, m. p. 28—31°, b. p. 183—185°/762 mm. The calcium salt, $(C_5H_7O_2)_2Ca$, crystallises in flat, rhombic needles; the silver salt, $C_5H_7O_2Ag$, forms thin needles or leaflets, apparently rhombic.

E. H. R.

Behaviour of Crotonic Acid in Ultra-violet Light. II. R. STOERMER and E. ROBERT (*Ber.*, 1922, 55, [B], 1030—1040; cf. Stoermer and Stockmann, A., 1914, i, 925).—It has been found previously that the transformation of crotonic into isocrotonic acid under the influence of the light from a Uviol lamp could not be established with certainty. By the use of the more powerful Heräus lamp, this transformation has been shown to occur to a small extent; on one occasion, it was found possible to isolate pure isocrotonic acid from the product, but, in general, the substance is separated as the corresponding amide. The experiments are rendered difficult by the restricted range of solvents available and the marked resinification which usually occurs, but is least obvious in toluene.

Under the influence of ultra-violet light, aniline and ammonia are very readily added at the double bond of $\alpha\beta$ -unsaturated acids. Thus crotonic acid and aniline give mainly β -anilinobutyric acid and anilinobutyranilide with minor amounts of croton- and isocroton-anilides, whereas the chief products with ammonia are β -aminobutyric acid and iminodibutyric acid, and, in addition, very small quantities of crotonamide. Crotonic acid and *p*-toluidine give β -*p*-toluidinobutyric acid, which could not be caused to crystallise and was therefore analysed as its *ethyl* ester, b. p. 186—188°/30 mm.; the latter yields a *hydrochloride* which crystallises with difficulty.

Acetic, propionic, and (to a less extent) benzoic acids are converted into their anilides when mixed with aniline and exposed to the light of the Heräus lamp; the action is shown to be due to the radiation and not to the temperature of the lamp. The formation of amides takes place with considerably greater difficulty.

H. W.

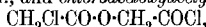
Erucic Acid and Erucic Anhydride. II. D. HOLDE and C. WILKE (*Z. angew. Chem.*, 1922, 35, 186—187; cf. this vol., i, 217).—Historical. The authors give an account of attempts by earlier workers to isolate pure erucic acid from rape oil, the successful conclusion of which in their hands has been already described (*loc. cit.*).

G. F. M.

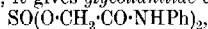
So-called Raptic Acid. ALFRED GRABNER (*Monatsh.*, 1921, 42, 287—292).—The acid known as rapic acid was first isolated by Reimer and Will (A., 1887, 1030) and was shown by Zellner to have the formula $C_{18}H_{34}O_2$ (A., 1896, i, 592) and to be probably an isomeride of oleic acid. It has now been submitted to detailed comparison with oleic acid and shown to be identical therewith.

E. H. R.

Action of Thionyl Chloride on α -Hydroxy-acids. E. E. BLAISE and (Mlle) MONTAGNE (*Compt. rend.*, 1922, **174**, 1173-1174).—Thionyl chloride reacts with glycollic acid, giving two products, namely, *Chlorosulphonylacetyl chloride*, $\text{SO}_2\text{Cl}\cdot\text{CH}_2\cdot\text{COCl}$, b. p. 78–82°/16 mm., and *chloroacetoxyacetyl chloride*,



b. p. 99–101°/17 mm. The former compound is very unstable, and on heating at 180° it decomposes, giving sulphur dioxide and chloroacetyl chloride. It is also decomposed by water or methyl alcohol. With aniline, it gives *glycollanilide sulphite*,



m. p. 140–141°. This sulphite also loses sulphur dioxide when heated, giving glycollanilide, which, with thionyl chloride, regenerates the sulphite. Chloroacetoxyacetyl chloride gives with aniline an *anilide*, m. p. 119°. W. G.

Oxidation of Dihydroxystearic Acid. YOSHIHIKO ASAHINA and YOSHIROYO ISHIDA (*J. Pharm. Soc. Japan*, 1922, 171–179).—Azelaic and *n*-nonoic acids are readily prepared from dihydroxystearic acid by oxidation. One part of dihydroxystearic acid (obtained by oxidation of oleic acid with potassium permanganate in potassium hydroxide solution) is added to a mixture of 2 parts of crystallised sodium dichromate and 25 parts of 25% sulphuric acid, and gradually heated on an oil-bath until the temperature has risen to 80°; the mixture is then distilled with steam, the temperature of the bath being maintained at 110–120°. The distillate is saturated with sodium chloride, extracted with ether, and rectified, when *n*-nonoic acid of b. p. 150°/20 mm. is obtained. The non-volatile residue is filtered while hot. On cooling the filtrate, impure azelaic acid crystallises. It is dissolved in concentrated sodium carbonate, or, better, sodium hydroxide solution, boiled until the accompanying coloured compound is destroyed, filtered, acidified, and crystallised, when white leaves, m. p. 128–132°, are obtained. From 504 grams of dihydroxystearic acid, 202.5 grams of azelaic acid and 130 grams of *n*-nonoic acid were obtained.

By the same method, 89 grams of azelaic acid and 41.5 grams of heptoic acid were prepared from 480 grams of the trihydroxystearic acid obtained from ricinolic acid by oxidation with potassium permanganate. K. K.

The Hydrolysis of the Mono- and Di-ethyl Esters of Diethyl-malonic Acid. PHILIPPE DUMESNIL (*Bull. Soc. chim.*, 1922, [iv], **31**, 320–324; cf. A., 1921, i, 391).—The author has repeated previous work (*loc. cit.*) under slightly different conditions, and has obtained confirmatory results. W. G.

Glutaconic Acid. II. P. E. VERKADE (*Rec. trav. chim.*, 1922, **41**, 208–223; cf. Verkade and Coops, A., 1920, i, 592).—A summary and extension of previously published work. Different methods of preparation of glutaconic acid (Conrad and Guthzeit, A., 1883, 311; Blaise, A., 1904, i, 10; Fichter and Dreyfus, A.,

1900, i, 426; von Pechmann and Jenisch, A., 1892, i, 147; von Pechmann, A., 1891, ii, 1457; Bucherer, A., 1890, i, 736) are shown to yield a substance of identical properties; no trace of the presence of an isomeride could be detected. Various methods of preparation of isomerides were attempted, but without success. The formula suggested by Perkin and Tattersall (T., 1905, 87, 361) and modified by Thorpe (T., 1912, 101, 871) is discussed and

the author suggests that $\text{CO}_2\text{H}-\text{CH}-\text{CH}-\text{CH}-\text{CO}_2\text{H}$ is the



best representation of the experimental evidence.

H. J. E.

Isomerism in the Glutaconic Acid Series. FRANZ FEIST (*Annalen*, 1922, 428, 25—40).—The evidence which has been accumulated by Thorpe and his co-workers during the past seventeen years is summarised. The author maintains his view that the isomerides in this series of acids are of the ordinary geometrical type, the difference, revealed by Thorpe's work, between the chemical relationship of these compounds and that subsisting between other maleoid and fumaroid acids being a difference of degree and not one of principle. The absence of a second form of glutaconic acid is readily explicable on the assumption that the double bond changes position (cf. following abstracts and this vol., i, 553).

C. K. I.

The Two β -Methylglutaconic Acids. FRANZ FEIST and PAUL KARL BREUER (*Annalen*, 1922, 428, 59—68).—Both the *cis*- (labile) and *trans*- (normal) forms of ethyl β -methylglutaconate yield *ozonides* which on hydrolysis give ethyl acetoacetate and ethyl glyoxylate (also acetone and oxalic acid). *cis*-Ethyl β -methylglutaconate readily absorbs chlorine, giving a *dichloride* ($\text{C}_{10}\text{H}_{16}\text{O}_4\text{Cl}_2$), b. p. 159—161°/12 mm., and a *trichloro*-compound ($\text{C}_{10}\text{H}_{15}\text{O}_4\text{Cl}_3$), b. p. 116·5°/0·57 mm., 130°/0·96 mm., 142·0°/1·70 mm., 155·0°/2·70 mm. The *dibromide*, b. p. 108°/0·11 mm., 116°/0·66 mm., 133°/2·20 mm., 154—156°/11 mm., 159—160°/13 mm., on condensation with ethyl sodiomalonate gives ethyl ethanetetra-carboxylate and *ethyl β -oxalyl-n-butyrate*, b. p. 125·3°/1·6 mm., 163°/5 mm. (cf. preceding abstract).

C. K. I.

$\alpha\beta$ -Dimethylglutaconic Acid. FRANZ FEIST and (in part) PAUL KARL BREUER (*Annalen*, 1922, 428, 68—75).—Neither the *cis*- (labile) nor *trans*- (normal) forms of $\alpha\beta$ -dimethylglutaconic acid undergo optical resolution with the help of brucine, strychnine, or quinine. The quinine salt of the *cis*-acid is crystalline (needles), and has the composition $\text{C}_7\text{H}_{10}\text{O}_4 \cdot 2\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2 \cdot 6\text{H}_2\text{O}$.

Ethyl *cis*- (labile) $\alpha\beta$ -dimethylglutaconate gives an oily *ozonide*, $\text{C}_{11}\text{H}_{18}\text{O}_8$, which on hydrolysis gives ethyl acetoacetate, ethyl methylacetoacetate, methyl ethyl ketone, and other products which were not identified. The *trans*- (normal) ester yields an oily *ozonide*, $\text{C}_{11}\text{H}_{18}\text{O}_{10}$, which on hydrolysis gives mainly ethyl acetoacetate, acetone, and acetic acid. To account for these

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results it appears to be necessary to assume three-carbon tautomerism as in the case of the β -phenyl- α -methylglutaconic esters (cf. preceding abstracts and this vol., i, 553). C. K. I.

Aleuritic Acid. C. HARRIES and W. NAGEL (*Chem. Umschau*, 1922, 29, 135—137).—The acid was obtained as potassium salt in 30% yield by allowing 5*N*-potassium hydroxide to act in the cold for twelve hours on shellac. After purification, the acid gave figures corresponding with the formula $C_{16}H_{32}O_5$, and molecular weight determinations confirmed this. The acid has m. p. 100—101°, and yields a *methyl* ester (colourless needles, m. p. 69—70°) and a *triacetyl* derivative, $C_{15}H_{28}(OAc)_3 \cdot CO_2H$, and when reduced by hydriodic acid yields palmitic acid. The acid is therefore a trihydroxypalmitic acid as suggested by Endemann and not dihydroxytridecoic acid as stated by Tschirch and Farnier (A., 1899, i, 447). H. C. R.

Action of Acids on Ammonium Molybdomalate. E. DARMOIS (*Compt. rend.*, 1922, 174, 1062—1064).—The ammonium molybdomalate, $2MoO_3 \cdot C_4H_4O_5(NH_4)_2$, is very sensitive to the action of acids. On the addition of small amounts of hydrochloric acid to its solution the rotation rapidly decreases to a limit value which is the same if nitric or sulphuric acids is used in place of hydrochloric acid. The limiting value of the rotation corresponds with the formation of the compound, $MoO_3 \cdot 2C_2H_5O_3$. If acetic acid is used, the action is not so marked and the results with this acid and its chloro-derivatives indicate that, in these cases, the diminution in rotation is proportional to the total quantity of hydrogen-ions. It is suggested that this difference may serve as the basis of a method for detecting the presence of mineral acid in acetic acid. W. G.

Preparation of Formaldehyde and Methyl Alcohol. H. OTTO TRAUN'S FORSCHUNGLABORATORIUM (Brit. Pat. 156148).—Formaldehyde and methyl alcohol are obtained by the oxidation of methane, or natural gas containing methane, by means of carbon dioxide, the mixed gases being passed through a constricted pipe heated at 500—700° at the constriction, and the gaseous reaction products rapidly cooled. The tube may be made of copper, silver, or nickel, or alloys of these metals with one another or with tin, zinc, aluminium, etc., which metals catalytically assist the reaction. If iron pipes are used, they are advantageously packed with wire or turnings of the above metals or alloys. The following reactions apparently occur in the process: $2CO = 2CO + 2O$ and $CH_4 + 2O = H \cdot CHO + H_2O$. The yield of formaldehyde under favourable conditions may amount to 56%, calculated on the methane employed. The yield of methyl alcohol is favoured by a slower passage of the gas through the tubes, and by the presence of hydrogen in the gas mixture. Saturation of the gases with alcohol vapour at 20—30° favourably influences the reaction. G. F. M.

Aptitude of Formaldehyde to Form Hydrocyanic Acid by Oxidation in Ammoniacal Silver Solutions. R. FOSSE and A. HIRULLE (*Compt. rend.*, 1922, **174**, 1021—1023; cf. this vol., i, 117).—By oxidising very small amounts of formaldehyde with excessive amounts of potassium permanganate in strong ammonium hydroxide in the presence of a silver salt and ammonium chloride the yield of hydrocyanic acid obtained may be as high as 37%. At the same time, however, a considerable amount of cyanic acid is produced.

W. G.

Preparation of Acetaldehyde from Acetylene. SHUICHIRO OCHI, VOICHI ONOZAWA, and THE TOKYO INDUSTRIAL LABORATORY (Japan. Pat. 38752, 1921).—Acetaldehyde is prepared by introducing 10.3 litres of acetylene into 100 c.c. of a solution containing 25 grams of sulphuric acid, 1 gram of mercuric oxide, and 3.6 grams of ferric acetate, and heating at 40° for three hours, the product being then distilled with steam.

K. K.

Researches on Residual Affinity and Co-ordination. VIII. Interaction of Tellurium Tetrachloride and β -Diketones. GILBERT T. MORGAN and HARRY DUGALD KEITH DREW [with E. A. COOPER] (*T.*, 1922, **121**, 922—940).

Electrolytic Reduction of Dextrose. ALEXANDER FINDLAY and VERNON HARCOURT WILLIAMS (*Trans. Faraday Soc.*, 1922, **17**, 453—456).—The method and apparatus used were those of Tafel (*A.*, 1900, ii, 588). A current density of 0.16 ampere per sq. dm. was employed, the solutions contained 1—10% of dextrose in 3% of sulphuric acid, the rate of absorption of hydrogen fell rapidly almost to zero, and the total amount absorbed corresponded with a 2% reduction of dextrose. The current concentration was varied between the limits of 0.04 and 0.444 ampere per 100 c.c. With increase of current concentration the absorption of hydrogen increases but falls off rapidly. No appreciable change was effected by changing the temperature, substituting gas carbon or Acheson graphite for lead electrodes or changing the current density. The rapid falling off of the hydrogen absorbed was found to be due to a film of lead formate formed on the cathode. The products of reduction were found to be formic acid and a pentose (cf. Löh, *A.*, 1910, i, 94); contrary to the claims of O'Brien Gunn [*D.R.-P.* 140318 (1900)], no hexahydric alcohol was formed.

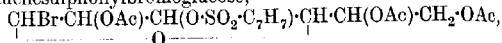
W. T.

The Catalytic Hydrogenation of Dextrose. W. E. CAKE (*J. Amer. Chem. Soc.*, 1922, **44**, 859—861).—When dextrose is hydrogenated in $N/2$ -potassium hydroxide solution in the presence of platinum black, *d*-sorbitol and *d*-mannitol are obtained.

W. G.

Syntheses of Mixed Acylated Halogen Sugars. KARL FREUDENBERG and OTTO IVERS (*Ber.*, 1922, **55**, [B], 929—941).—The authors have attempted the synthesis of substances of the type of acetobromoglucose in which the individual acetyl groups

are replaced by other acyl radicles. The preparation of triacetyl-*p*-toluenesulphonylbromoglucose,



is now described, the initial material being dextrosediactone (cf. Fischer and Rund, A., 1916, i, 364).

A simplified method for the preparation of dextrosediactone consists in shaking β -glucose (Behrend, A., 1907, i, 481; 1911, i, 14) with acetone containing a little hydrogen chloride at the atmospheric temperature and subsequent neutralisation of the acid by the addition of 5*N*-sodium hydroxide solution; the bulk of the acetone is removed by distillation on the water-bath and the remainder under diminished pressure. The dextrosediactone is removed from the residue by treating it with warm light petroleum. It is converted by toluene-*p*-sulphonyl chloride in the presence of aqueous potassium hydroxide solution or pyridine into *toluene-p-sulphonyldextrosediactone*, slender needles, m. p. 120—121°, $[\alpha]_D^{20}$ —81.7° in *s*-tetrachloroethane; the latter substance is remarkably stable towards warm concentrated alcoholic alkali hydroxide solutions and is unaffected by ammonia at 100°. Warm dilute sulphuric acid causes the successive removal of the acetone residues and the toluene-*p*-sulphonyl group, so that by interrupting the reaction at the requisite moment it is possible to isolate 3-*toluene-p-sulphonyldextrose* (the constitution assigned to this compound is necessarily dependent on the correctness of the formulation of dextrosediactone); the substance crystallises as the monohydrate, m. p. (indefinite) 70—71° after softening at 65—66°, $[\alpha]_D^{20}$ +39.64° in aqueous solution. It is re-converted by acetone and hydrogen chloride into toluene-*p*-sulphonyldextrosediactone. Treatment of toluene-*p*-sulphonyldextrose with pyridine and acetic anhydride leads to the formation of *toluene-p-sulphonyltetra-acetylglucose*, m. p. 170—171° (decomp.), $[\alpha]_D^{20}$ +13.6°, when dissolved in *s*-tetrachloroethane. The tetra-acetyl derivative is converted by glacial acetic acid and hydrogen bromide or by liquid hydrogen bromide into *toluene-p-sulphonyltriacytylbromoglucose*, slender needles, m. p. 150—151°, $[\alpha]_D^{20}$ +164.4°, which can also be prepared directly from toluene-*p*-sulphonyldextrosediactone, glacial acetic acid, and hydrogen bromide; it is re-converted by a solution of thallium acetate in acetic acid and acetic anhydride into toluene-*p*-sulphonyltetra-acetyldextrose. *Toluene-p-sulphonyltriacytylmethylglucoside*, slender needles, m. p. 138°, $[\alpha]_D^{20}$ —17.1° in *s*-tetrachloroethane is prepared by agitating a solution of the bromo-compound in methyl alcohol with silver carbonate.

Benzoyltriacytylbromoglucose, m. p. 152°, $[\alpha]_D^{20}$ +162.5° when dissolved in *s*-tetrachloroethane, is prepared by the action of glacial acetic acid and hydrogen bromide on benzoyldextrose-diacetone (Fischer and Noth, *loc. cit.*).

An improved method is given for the preparation of octa-acetyl-maltose. When dissolved in benzene, it is converted by a saturated solution of hydrogen chloride in anhydrous ether into a crystalline substance, m. p. 112—114°, $[\alpha]_D^{20}$ +67.5° in chloroform, which

appears to be an octa-acetylchloromaltose; the chlorine atom is displaced with unusual readiness.

The estimation of readily eliminable halogen is conveniently effected by boiling a solution of the substance in glacial acetic acid with a similar solution of thallium carbonate. The thallium haloid which is quantitatively precipitated is filtered through a Gooch crucible, washed with hot glacial acetic acid, dried at 135–140°, and weighed.

H. W.

Thioglucose. FRITZ WREDE (*Z. physiol. Chem.*, 1922, **119**, 46–59).—Boiling potassium disulphide solution converts tetra-acetylbromoglucose into octa-acetyldithiodiglucose (Wrede, A., 1920, i, 13), and this, on reduction at a temperature below 25° with sodium amalgam in alcohol containing acetic acid, gives *tetra-acetylthioglucose*, which crystallises in thick, compact masses, m. p. 75°; $[\alpha]_D^{25}$ –13.57°, in 90% alcohol, after seven days, –6.78°; $[\alpha]_D^{25}$ +0.5° in $\alpha\alpha\beta\beta$ -tetrachloroethane. Tetra-acetylthioglucose quickly changes Fehling's solution in the cold and gives a dark-coloured precipitate on boiling. On long exposure to the air, but quickly if hydrogen peroxide be added, it is reconverted into octa-acetyldithiodiglucose. With diazomethane in ethereal solution, tetra-acetyl- β -methylthioglucoiside is formed, compact crystals from methyl alcohol, m. p. 95°, $[\alpha]_D^{25}$ –16.18° in $\alpha\alpha\beta\beta$ -tetrachloroethane. By acetic anhydride, it is converted into *penta-acetylthioglucose*, white, compact needles, m. p. 121°, $[\alpha]_D^{25}$ +1.6° in ethyl acetate. This substance is also obtained directly from octa-acetyldithiodiglucose on reduction with zinc dust and acetic anhydride. Penta-acetylthioglucose, on hydrolysis by methyl alcohol saturated with ammonia, is converted into *thioglucose*, which can also be obtained in a less pure condition by the reduction of octa-acetyldithiodiglucose with aluminium amalgam or sodium amalgam in alcoholic solution containing acetic acid. It has not been found possible to recrystallise thioglucose. After drying over phosphoric oxide in a vacuum, it is an amorphous, white powder, sintering at 70° and foaming at 105°. It shows mutarotation: $[\alpha]_D^{25}$ +23° in 50% alcohol when equilibrium is reached. Its solubility is similar to that of dextrose; its taste is unpleasant and scarcely sweet. Fehling's solution gives a green colour in the cold, which does not increase on heating. It forms a *silver* salt, $C_6H_{11}O_5Ag$, a yellowish-white non-hygroscopic powder, which can be decomposed by methyl iodide to give β -methylthioglucoiside isolated as its tetra-acetyl derivative.

W. O. K.

The Polymerisation of Lævoglucosan. AMÉ PICTET and J. H. ROSS (*Compt. rend.*, 1922, **174**, 1113–1114; A., 1921, i, 647, 766).—When lævoglucosan is heated with a trace of zinc chloride at 140°, the reaction $nC_6H_{10}O_5 = (C_6H_{10}O_5)_n$ takes place in a few minutes, but the products of the reaction vary with the pressure. As the pressure increases the value of n increases. Thus at a pressure of 15 mm. the product is a *dilævoglucosan*, m. p. 135°, $[\alpha]_D^{25}$ +28.2°; at the atmospheric pressure the product is *tetralævoglucosan*, $[\alpha]_D^{25}$ +111.9°; at a pressure of 4.6 atmos. *hexalævoglucosan*,

$[\alpha]_D +94.1^\circ$, is obtained, and at 13.3 atmos. *octalævoglucosam*, $[\alpha]_D +72.8^\circ$, is the product. As the polymerisation increases, the products have properties more nearly approaching those of the dextrans.

W. G.

Celloisobiose. H. OST and G. KNOTH (*Cellulosechemie*, 1922, 3, 25—38).—*Celloisobiose* is a well-characterised biose sugar the *octa-acetate* of which occurs in the products of acetolysis of cellulose, but readily undergoes conversion into the more stable cellobiose-*octa-acetate*. The *octa-acetates* are partly separable by extracting the crude product of acetolysis with ether and then extracting the extracts with alcohol. The *isobiose acetate* is concentrated in the fractions which are readily soluble both in ether and in alcohol. The biose itself is isolated by saponifying the acetate fraction with $N/2$ -barium hydroxide at 25° and submitting the syrup to a systematic fractionation with aqueous alcohol of 85—100% strength. The major portion occurs in the fractions soluble in 85% alcohol. A yield of 2.5 parts of purified *isobiose* per 100 of cellulose was thus isolated, but, owing to the instability of its acetate, the quantity originally formed must have been much larger. *Celloisobiose* crystallises in microscopic needles with $\frac{1}{2}H_2O$; after drying at 105° , the crystals break down to a powder. It is hydrolysed more slowly than most other bioeses into 2 mols. of dextrose. It shows multirotation, which arrives at a constant value of $[\alpha]_D^{20} +24.6^\circ$ after six hours in 6—8% solution. It has a cupric-reducing value equivalent to 63.2% of dextrose, and forms an *osazone* melting at 165 — 167° , with a composition indicating one free aldehyde group. The authors consider that the cellulose molecule is probably built up entirely of biose units, and that their crude acetates derived directly from the cellulose apparently contained 40% of cellobiose *octa-acetate*, 40% of *isobiose octa-acetate*, and about 15% of acetates of cellulose dextrans, which themselves would presumably have given further quantities of biose acetates if the reaction had been more complete. J. F. B.

The Heat Developed by the Action of Sodium Hydroxide on Cotton ("Mercerisation"). THOS. BARRATT and J. W. LEWIS (*Trans. Text. Inst.*, 1922, 13, 113—120).—As a contribution to the problem of the connexion between the concentration of sodium hydroxide employed and the "degree of mercerisation" produced, which has not yet received any satisfactory solution, the authors have measured the heat developed when well-scoured Egyptian cotton is immersed in solutions of sodium hydroxide of various concentrations. Since the heat developed is not great (the greatest rise in temperature being 0.5°) and equilibrium is only reached after several minutes in certain cases, an electrical system was elaborated by means of which heat development was measured directly and such factors as the specific heat of the liquid and the total thermal capacity of the calorimeter and its contents could be neglected. The apparatus is fully described, and it is stated that it would also serve for a study of heats of dilution.

A small correction was applied for the heat of dilution of the alkali by the water present in the cotton. This amounted to 5.1%, the material being kept for several months in a desiccator over sulphuric acid (d 1.345), at nearly constant temperature, in order to control the moisture content. The "heat of mercerisation" increases with the concentration of the sodium hydroxide solution, but is not proportional to it. The curve shows an inflection corresponding with a rapid increase in the heat produced when the concentration of alkali is between 10% and 15%, which is the lower limit of the commercial mercerising process. A second inflection, corresponding with a decrease, occurs at about 30%, which is near the upper limit of solutions usually employed in the industry. The rate at which heat is developed is greatest between about 10% and 18%, equilibrium being reached in solutions within these concentrations in about two minutes. J. C. W.

Compounds of Iodine with Constituents of Starch. H. VON EULER and KARL MYRBÄCK (*Annalen*, 1922, 428, 1—24).—This paper records a large number of measurements of the partition coefficient of iodine between benzene and starch obtained from various sources and previously treated in different ways. The general inference is that two compounds are formed probably with the amylose, and the formulæ $(C_6H_{10}O_5)_{12}I_2$ and $(C_6H_{10}O_5)_{12}I_4$ are suggested with reservations. The formation of these substances is reversible, and is controlled by a dissociation pressure for each which is constant for a constant temperature, although above 40° the formation of hydriodic acid becomes perceptible.

Starch-iodide can be titrated with sodium hydroxide, one atom of iodine being equivalent to about 7NaOH. On back-titration with acids, the iodine is again liberated and forms starch-iodide, one atom of iodine being set free for each 4NaOH neutralised. C. K. I.

Amylocellulose considered as Composed of Silicic Acid and Amylose. G. MALFANO and M. CATOIRE (*Compt. rend.*, 1922, 174, 1128—1130).—The authors suggest that the resistance to the action of hot water or acids shown by that part of the starch grain known as amylocellulose is due to the presence of silicic acid and that this material is really a complex compound of amylose with silicic acid of the type $[SiO_3(C_6H_{10}O_5)_n]H_2$. They consider that the various amylaceous materials may be looked on as complexes of silicic acid, phosphoric acid, or simply water with the group $C_6H_{10}O_5$, and that this theory is in better accord with the experimental facts than that which demands varying stages of polymerisation and condensation. W. G.

Chlorites of Ammonium, Tetramethylammonium, and certain Amines. GIORGIO RENATO LEVI (*Gazzetta*, 1922, 52, i, 207—209; cf. A., 1916, ii, 27).—*Ammonium chlorite*, NH_4ClO_2 , forms transparent, pale yellow, prismatic needles, is not deliquescent, decomposes rapidly when heated, and is exploded by percussion on an anvil. *Methylamine chlorite*, $NH_2Me.HClO_2$, is obtainable only in 66–67% aqueous solution, which detonates

slightly when poured on to a hot iron plate. *Dimethylamine chlorite*, $\text{NHMe}_2\text{HClO}_2$, and *trimethylamine chlorite*, $\text{NMe}_3\text{HClO}_2$, also obtainable only in aqueous solution, behave similarly to the previous compound, the tertiary compound exhibiting greater tendency to decompose on concentration. *Tetramethylammonium chlorite*, NMe_4ClO_2 , forms colourless crystals, is highly deliquescent, explodes on percussion, and forms neutral aqueous solutions.

T. H. P.

Preparation of Hexamethylenetetramine and Formaldehyde

H. OTTO TRAUN'S FORSCHUNGS-LABORATORIUM (Brit. Pat. 156136).—Formaldehyde can be obtained in satisfactory yield by the contact oxidation of methane (or natural gas containing methane) if the oxidation takes place in presence of ammonia whereby the more stable hexamethylenetetramine is formed and the aldehyde is thus saved from destruction. For example, a mixture of 6 vols. of methane, 12 vols. of oxygen, and 4 vols. of ammonia is passed through a reaction tube provided with a constriction, where it is heated at $300\text{--}500^\circ$, or even at 700° if the reaction is performed under reduced pressure. The tube itself may serve as the catalyst, or a steel or iron tube packed at the constriction with silver, nickel, or copper wire may be used. The reaction product is condensed and consists mainly of hexamethylenetetramine (70% yield), from which formaldehyde can be regenerated in known manner. The yields are favourably influenced by saturating the gases with methyl or ethyl alcohol vapour before passing them through the contact tube.

G. F. M.

The Two Modifications of Glycine. Methylation with Diazomethane. HEINRICH BULTZ and HANS PAETZOLD (Ber., 1922, 55, [B], 1066—1073).—The occurrence of two modifications of glycine has been noted by Fischer (A., 1905, i, 863) and Falk and Sugiura (A., 1918, i, 292); according to the former, the yield of aminoacetyl chloride hydrochloride from glycine depends on whether the plate or needle variety of the latter is used, whilst, according to the latter, the two modifications behave differently when heated and have differing additive capacity towards bromine. The explanation is now found in the observation that the large plate-like crystals deposited from aqueous solution enclose mother-liquor which is not removed even when the finely divided material is heated at 100° . This can be effected at 130° , and the behaviour of both crystalline forms becomes then physically and chemically identical. Alanine behaves in a similar manner. When heated glycine decomposes at about 245° after becoming brown at about 220° and black at about 237° . Either form absorbs bromine vapour to an equal degree under identical conditions, but the actual amount depends greatly on the tension of the bromine vapour, and there does not appear to be any indication of the formation of a definite product. The absorbed bromine is evolved completely when the products are prepared over moistened potassium hydroxide.

Neither variety is methylated appreciably by an ethereal solution of diazomethane, such action as is observed being due to the

methylation of admixed methyl alcohol, which can also be catalysed by other agents. The addition of a small quantity of water causes the reaction to proceed vigorously with the formation of betaine in about 75% yield from either variety; the action of the water is attributed to its solvent power towards glycine.

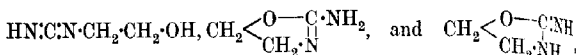
H. W.

Preparation of Dialkylaminoalkyl Compounds. FARBERKE FORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 167781; from *Chem. Zentr.*, 1921, iv, 1223).—Halogen alkylalkylamines are allowed to react with alkali salts of compounds of the general formula $R\text{-CO-CHR}'X$, where R and R' are hydrogen or an organic radicle and X is a negative group such as $\text{—CO}_2\text{Et}$, —COMe , —Bz , or —CN . Such compounds are ethyl acetoacetate, ethyl cyanoacetate, ethyl malonate, ethyl acetonedicarboxylate, ethyl camphorcarboxylate, ethyl succinylsuccinate, or acetylacetone. Dialkylaminoalkyl compounds can also be prepared by the action of dialkylamines on halogen derivatives of the compounds mentioned. *Ethyl α -diethylaminoethylacetoacetate* is prepared from ethyl sodioacetoacetate and chloro- or bromo-ethyldiethylamine, or from ethyl α -bromoethylacetoacetate and diethylamine. By similar methods, the following compounds are obtained: *methyl α -diethylaminoethylacetoacetate*; *ethyl α -dimethylaminoethylacetoacetate*; *ethyl diethylaminobutylacetoacetate*; *ethyl diethylaminoethylmalonate*; *ethyl diethylaminoethylcyanoacetate*; *ethyl bisdiethylaminoethyldiketocyclohexanedicarboxylate* (from diethylchloroethylamine and ethyl sodium succinylsuccinate); *ethyl diethylaminoethylacetonedicarboxylate*; *methyl diethylaminoethylcamphorcarboxylate*; *diethylaminoethylacetylacetone*. *Diethylchloroethylamine* is obtained by the action of thionyl chloride on diethylaminoethanol in chloroform solution and decomposition of the hydrochloride with potassium carbonate. *Diethylbromoethylamine* is obtained by heating diethylaminoethanol hydrobromide with 48% hydrobromic acid. *Diethylchlorobutylamine*, $\text{NEt}_2\text{[CH}_2\text{]}_3\text{CHMeCl}$, is obtained by the reduction of diethylaminobutanone to the corresponding alcohol and subsequent treatment with thionyl chloride. *Diethylpiperazine dichloroethylate* is obtained as a by-product in the preparation of ethyl α -diethylaminoethylacetoacetate. G. W. R.

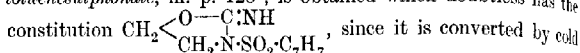
Synthesis of Formamide from Carbon Monoxide and Ammonia. KURT H. MEYER and LUDWIG ORTHNER (*Ber.*, 1922, 55, [B], 857; cf. A., 1921, i, 775).—A correction in the calculation of the equilibrium constant.

H. W.

Synthesis with Cyanamide. **Cyanamidoethyl Alcohol and Guanidoethyl Alcohol.** EMIL FROMM and ERNST HONOLD (*Ber.*, 1922, 55, [B], 902—911).—*Cyanamidoethyl alcohol*, an oily liquid which could neither be caused to crystallise nor distilled without decomposition even in a vacuum, is prepared by the action of ethylene chlorohydrin on an aqueous solution of sodium cyanamide and is characterised by its benzoate and *p*-toluenesulphonate. The substance can react in the following forms, $\text{NC}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$,

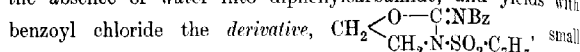


and its derivatives are constituted differently from one another. With toluene-*p*-sulphonyl chloride in the presence of alkali, a *mono. toluenesulphonate*, m. p. 128°, is obtained which doubtless has the



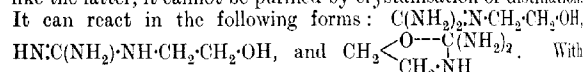
dilute sulphuric acid with loss of ammonia into 3-*p*-toluenesulphonyl.

1 : 3-oxazolid-2-one, m. p. 193°, is transformed by aniline even in the absence of water into diphenylcarbamide, and yields with

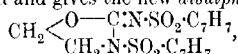


needles, m. p. 117°, which is converted by cold dilute sulphuric acid into benzoic acid, ammonia, and the lactone, m. p. 193° (see above). Cyanamidoethyl alcohol is converted by benzoyl chloride in alkaline solution into a *dibenzoyl* derivative, colourless needles, m. p. 165°, to which the constitution $\text{NBz}:\text{C}:\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OBz}$ is assigned. It is completely stable towards dilute sulphuric acid, but is transformed by cold, concentrated sulphuric acid and subsequent addition of water into *benzoyl-β-benzoxylethylcarbamide*, $\text{NHBz} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OBz}$, m. p. 176°. It is converted by aniline into benzanilide and *benzoylphenylcarbamide*, lustrous platelets, m. p. 204°. Finally, when a boiling alcoholic solution of dibenzoylcyanamidoethyl alcohol is treated with ammonia *dibenzoyl-β-hydroxyethylguanidine*, $\text{NHBz}:\text{C}(\text{NH}_2):\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OBz}$, thin needles, m. p. 150°, is produced from which benzoylcarbamide is readily isolated by the action of dilute hydrochloric acid in the presence of alcohol; it is remarkable that the guanidine derivative cannot be benzoylated further by the Schotten-Baumann method.

Guanidoethyl alcohol is prepared by passing gaseous ammonia into the boiling alcoholic solution of cyanamidoethyl alcohol; like the latter, it cannot be purified by crystallisation or distillation. It can react in the following forms: $\text{C}(\text{NH}_2)_2 \cdot \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$,



With benzoyl chloride, it gives a *tribenzoate*, $\text{C}(\text{NHBz})_2 \cdot \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OBz}$, m. p. 156°, which is hydrolysed smoothly by dilute hydrochloric acid in alcoholic solution to dibenzoylcarbamide, m. p. 197°. With toluene-*p*-sulphonyl chloride and sodium hydroxide, it yields a *disulphonate*, $\text{N}(\text{SO}_2 \cdot \text{C}_6\text{H}_5):\text{C}(\text{NH}_2):\text{N}(\text{SO}_2 \cdot \text{C}_6\text{H}_5) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, lustrous platelets, m. p. 163°, which loses ammonia, without, however, adding the elements of water under the action of boiling dilute sulphuric acid and gives the new *disulphonate*,



m. p. 206°.

H. W.

The Action of Sulphuric Acid on Nitroguanidine. TENNEY L. DAVIS (*J. Amer. Chem. Soc.*, 1922, **44**, 868—872).—Nitroguanidine is decomposed quantitatively by hot concentrated

sulphuric acid, half of its nitrogen being liberated as ammonia and the whole of its carbon as carbon dioxide.

Solubility curves of nitroguanidine in sulphuric acid of varying strengths at 0° and 25° have been constructed. W. G.

Synthesis and Properties of Tetramethylenediguandine.

ALEXANDER KIESEL (*Z. physiol. Chem.*, 1922, **118**, 277—283).—In repeating the synthesis by Kossel (A., 1910, i, 500, 625) of agmatine (α -amino- δ -guanidino-*n*-butane), by the action of cyanamide on tetramethylenediamine (putrescine), the author has improved the yield, and has obtained also from the product of the reaction *tetramethylenediguandine*, $C_4H_8[NH \cdot C(NH) \cdot NH_2]_2$ as its *sulphate*, spherical aggregates of needles, m. p. 291° (decomp.). The following salts have also been prepared: *carbonate*, small, thick prisms or boat-shaped crystals; *hydrochloride*, thick, transparent prisms; *picrate*, small, thin, light yellow prisms, m. p. 253—254° (decomp.); *picrolonate*, yellow, amorphous, m. p. 278—279° (decomp.); *aurichloride*, small, lustrous needles, m. p. 172.5°, and *platinichloride*, orange, rhombic plates or feather-like, crystalline aggregates, m. p. 224° (decomp.). W. O. K.

The Action of the Grignard Reagent on Thiocyanates.

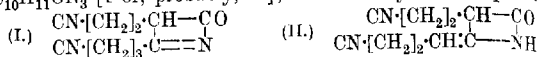
ROGER ADAMS (*J. Amer. Chem. Soc.*, 1922, **44**, 873).—Certain structural formulæ given in a previous paper are now corrected (cf. A., 1921, i, 5). W. G.

Preparation of Ethylene Cyanohydrin [β -Hydroxypropionitrile]. RÖHM and HAAS (Fr. Pat. 525539; from *Chem. Zentr.*, 1921, iv, 1222).—The reaction of ethylene halogen-hydrins and cyanide solutions takes place in aqueous solutions at temperatures below the temperature at which the cyanohydrin is decomposed by aqueous salt solutions. For example, *ethylene cyanohydrin* is formed by the reaction of ethylene bromohydrin with potassium cyanide solution at 55—60°. Ethylene chlorohydrin reacts similarly with sodium cyanide solution; 85—95% of the theoretical yield is obtained. G. W. R.

The Action of Organo-magnesium Compounds on Glutaronitrile.

P. BRUYLANTS (*Bull. Acad. roy. Belg.*, 1921, [5], **7**, 252—259; from *Chem. Zentr.*, 1921, iii, 1349; cf. Blaise, A., 1921, i, 647).—By the action of magnesium ethyl bromide on glutaronitrile, ethane is evolved with the probable formation of a compound, $CN \cdot CH_2 \cdot CH_2 \cdot CH \cdot CN \cdot MgBr$, which when decomposed by acidified water gives exclusively glutaronitrile and glutaramide nitrile (?). By heating the nitrile (1 mol.) with magnesium ethyl bromide (2 mols.) and decomposing with water, small quantities of a *ketone*, probably $COEt \cdot [CH_2]_3 \cdot CN$, a liquid of camphor-like odour, b. p. 170°/17 mm., are obtained; the *semicarbazone* has m. p. about 215°. The hydrolysis of the *ketone* with hydrochloric acid gives *propionylbutyric acid* (?). The decomposition with water of the magnesium compound formed from an equimolecular mixture of glutaronitrile with a mag-

nesium methyl, ethyl, or propyl haloid gives a compound, $C_{10}H_{11}ON_3$ [I or, probably, II]; it forms crystals, m. p. 149-6.



149-8°; molecular weight in acetic acid 100-110. It reacts energetically with 1 molecule of bromine, giving 1 molecule of hydrogen bromide. By hydrolysis with hydrochloric acid, an acid, $\text{CO}([\text{CH}_2]_3 \cdot \text{CO}_2\text{H})_2$, is formed, having m. p. 91-93°.

G. W. R.

Crystal Structures of Complex Cyanides of Potassium with Zinc, Cadmium, and Mercury. ROSCOE G. DICKINSON (*J. Amer. Chem. Soc.*, 1922, 44, 774-784).—The crystal structures of potassium zinc cyanide, $\text{K}_2\text{Zn}(\text{CN})_4$, potassium cadmium cyanide, $\text{K}_2\text{Cd}(\text{CN})_4$, and potassium mercury cyanide, $\text{K}_2\text{Hg}(\text{CN})_4$, have been determined by X-ray spectral photographs and unsymmetrical Laue photographs. It is shown that the theory of space groups is extremely useful in interpreting the experimental data, and also that it was not necessary to make any quantitative assumptions as to the "normal decline" of intensity. All three substances have a cubic structure. The following data are recorded: potassium zinc cyanide, length of side of unit cube (d_{100}) = 12.54 Å., distance between potassium and cyanogen 3.20 Å.U., distance between zinc and cyanogen, 2.61 Å.U.; potassium cadmium cyanide, d_{100} = 12.84 Å.U., distance between potassium and cyanogen, 3.28 Å.U., distance between cadmium and cyanogen, 2.67 Å.U.; potassium mercury cyanide, d_{100} = 12.76 Å.U., distance between potassium and cyanogen, 3.25 Å.U., distance between mercury and cyanogen, 2.65 Å.U. The unit cube in all cases contains eight molecules. It is shown that these complex cyanides have the same structure as magnetite and spinel.

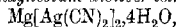
J. F. S.

Attempts to Prepare Pure Calcium Cyanide. HEINRICH PISCASS (*Chem. Ztg.*, 1922, 46, 347).—Pure calcium cyanide cannot be prepared by Schulz's method, which consists in mixing concentrated solutions of potassium ferrocyanide and calcium chloride, ignition of the precipitate at a dull red heat, and extraction of the residue with water. The action of hydrocyanic acid on calcium hydroxide in aqueous solution gives a product containing about 33% of calcium cyanide. At the atmospheric temperature, gaseous hydrocyanic acid and solid calcium hydroxide give the substance $3\text{Ca}(\text{OH})_2 \cdot 2\text{Ca}(\text{CN})_2 \cdot 13\text{H}_2\text{O}$ with 41% of calcium cyanide, whereas at 600-700° they give carbon, and calcium cyanide and cyanamide. If carbonisation is excluded by working in a vacuum, calcium cyanide alone is formed. The absorption of gaseous hydrocyanic acid by lime increases up to 300°, and then falls; at 700°, the formation of cyanide does not take place.

H. W.

Magnesium Cyanide. FR. FICHTER and RICHARD STIER (*Helv. Chim. Acta*, 1922, 5, 396-400).—Solutions of magnesium cyanide are best prepared by solution of the metal in 10-15%

aqueous hydrocyanic acid solution, but they gradually deposit the hydroxide even when preserved in an atmosphere of hydrogen cyanide. Contrary to the statement of Schulz (1856), the cyanide cannot be obtained in the crystalline condition by concentration of its solution. By addition of silver nitrate solution until a permanent turbidity is produced, filtration, and concentration in a vacuum, leaflets of *magnesium disilver tetracyanide*,



are isolated. By recrystallisation of this salt, and accompanying it, needles of *magnesium silver tricyanide*, $\text{Mg}[\text{Ag}(\text{CN})_2]$, are obtained. Dry magnesium hydroxide does not react with an ethereal solution of hydrogen cyanide (cf. Meyer, A., 1921, i, 501); in presence of moisture, a product is obtained which has suffered almost complete hydrolysis. The preparation of the anhydrous cyanide by heating magnesium ferrocyanide (analytical data for which indicate its existence in varying degrees of hydration) (Eidmann, A., 1899, i, 317) is unsatisfactory, not only on account of the presence of iron carbide and carbon in the product, but also owing to simultaneous formation of magnesium nitride: $3\text{Mg}_2[\text{Fe}(\text{CN})_6] = 2\text{Mg}_3\text{N}_2 + 3\text{FeC}_2 + 7\text{N}_2 + 15\text{C}$. This decomposition occurs to an extent which rapidly increases with rise in temperature above 400° , so that at 800° it is the sole reaction. The most favourable yields of cyanide (4.6–5.7 per cent.) were obtained at 450° .

J. K.

The Atomic Vibrations in the Molecules of Benzenoid Substances. R. ROBINSON (*Nature*, 1922, 109, 476).—If, in the annexed formula, it is assumed (Bragg, *Proc. Physical Soc.*, 1921, 34, 33) that the centres of the carbon atoms at *h*, *l*, *b*, *g*, *e*, and *c* lie in a plane, whilst those at *k* and *a* lie above the plane, and those at *f* and *d* an equal distance below it, enantiomorphism would result in the case of all mono-substituted and in the majority of the higher substituted compounds.

It is suggested that the above conception represents merely a phase of an oscillation of the relatively unrestricted molecules of the fused or dissolved substance in which the pairs of carbon atoms, *k*, *a*, and *f*, *d*, appear alternately above and below the plane containing the six remaining atoms. An identical result is obtained if all the atoms are supposed to be in motion in such a way that adjacent atoms move in opposite directions and to an equal distance from the plane of the original ring.

A. A. E.

Configurations of Molecules of Benzenoid Substances. J. KENNER (*Nature*, 1922, 109, 581; cf. preceding abstract).—Recent investigations (T., 1922, 121, 614) indicate that in the case of 6:6'-dinitrodiphenic acid, the two benzene nuclei in separate molecules (as distinguished from their crystalline aggregates, to which Bragg's results apply) are not coplanar. If this be so, it follows that the direction of the valency of each of the carbon atoms through which these nuclei are united is not, as represented



in the usual formula for benzene, exerted in the plane of the benzene ring, and, further, that this condition is a stable one, rather than a phase of an oscillation as suggested by Robinson. It is pointed out that one phase of Bloch's formula for benzene corresponds closely with that deduced by Bragg from observations on diamond and on naphthalene and its derivatives. A. A. E.

Ethylenic Stereoisomerism. CH. DUFRAISSE (*Ann. Chim.*, 1922, [ix], 17, 133—221).—A more detailed account of work already published (A., 1914, i, 845; 1920, i, 486; 1921, i, 17, 104, 114, 168; this vol., i, 39). W. G.

Oxidation of the Trinitroxylenes. M. GIUA (*Gazzetta*, 1922, 52, i, 183—188).—When oxidised by means of chromic acid, 3:4:6-trinitro-*o*-xylene and 2:3:5-trinitro-*p*-xylene yield, respectively, 3:4:6(or 3:5:6)-trinitro-*o*-toluic and 2:3:5-trinitro-*p*-toluic acids. By excess of chromic acid 2:4:6-trinitro-*m*-xylene in concentrated sulphuric acid solution is converted into 2:4:6-trinitroisophthalic acid.

3:4:6(or 3:5:6)-Trinitro-*o*-toluic acid, $\text{C}_6\text{H}_3\text{C}_6\text{H}_4\text{Me}(\text{NO}_2)_3$, crystallises in white needles, m. p. 201—202°, and gives a reddish-brown coloration with alkali; its silver salt deflagrates when heated.

2:4:6-Trinitroisophthalic acid, $\text{C}_6\text{H}(\text{NO}_2)_3(\text{CO}_2\text{H})_2$, forms white needles, m. p. 196—197° (evolution of gas), has a slightly bitter taste, and loses carbon dioxide with formation of *s*-trinitrobenzene when heated above its melting point or boiled with water.

2:3:5-Trinitro-*p*-toluic acid, $\text{C}_6\text{H}_3\text{O}_6\text{N}_3$, crystallises in lustrous, white lamellae, m. p. 230—231°, and gives a brownish-red coloration with alkali hydroxides. Its silver salt, which deflagrates when heated, methyl ester, white needles, m. p. 114—115°, and ethyl ester, colourless prisms, m. p. 87—88°, were analysed.

Methyl 3:5-dinitro-2-amino-*p*-toluate, $\text{C}_9\text{H}_9\text{O}_6\text{N}_3$, prepared by the action of alcoholic ammonia solution on methyl 2:3:5-trinitro-*p*-toluate, forms lustrous, yellow needles, m. p. 139—140°, and methyl 3:5-dinitro-2-ethylamino-*p*-toluate, $\text{C}_{11}\text{H}_{13}\text{O}_6\text{N}_3$, similarly obtained by the action of ethylamine, in yellow needles, m. p. 103—104°, which are slowly reddened by the action of light.

T. H. P.

An Instance of the Apparent Effect of the Entering Group on the Position of Substitution in the Benzene Nucleus. WILLIAM DAVIES (T., 1922, 121, 806—815).

The Cumulative Effect of the Chlorine Atom and the Methyl and Sulphonyl Chloride Groups on Substitution in the Benzene Nucleus. III. WILLIAM DAVIES (T., 1922, 121, 785—791).

Determination of the Configuration of the Stereoisomeric Hexamethylenes. A. SKITA (*Annalen*, 1922, 427, 255—280).—Most of this work has already been described (cf. A., 1921, i, 503). *cis*-1-Amino-*cis*-2-*trans*-4-dimethylcyclohexane is characterised by an acetyl derivative, b. p. 149°/12 mm., m. p. 29°, a phenylcarbamide, m. p. 60°, a *s*-thiocarbamide, $\text{C}_{17}\text{H}_{32}\text{N}_2\text{S}$, m. p. 182°, a picrate,

leaflets, m. p. 176–177°, and a *hydrochloride*, needles, m. p. 223°. The five corresponding derivatives of *cis*-1-amino-*trans*-2-*cis*-4-dimethylcyclohexane have the following m. p.: 120°, 128°, 215°, 155–156°, and 235°, respectively. C. K. I.

Catalytic Preparation of Aniline. II. O. W. BROWN and C. O. HENKE (*J. Physical Chem.*, 1922, 26, 272–287; cf. this vol., i, 445).—The reduction of nitrobenzene by hydrogen to aniline in the presence of various catalysts has been investigated. It is shown that cobalt is active at a lower temperature than nickel (*loc. cit.*), but it is to be noted that the cobalt contained a little nickel and the nickel a little cobalt. Iron is found to carry the reduction further than copper, but cannot be used below 300°, and at this temperature its action is too vigorous, the reduction being carried too far. Silver is an excellent catalyst, even better than copper prepared by ignition of the nitrate, because it may be used with a much higher rate of flow of nitrobenzene. Antimony, manganese, and chromium also act as catalysts in the reduction of nitrobenzene. The lower oxides of molybdenum, vanadium, uranium, tungsten, and cerium also catalyse the reduction. The activity of the oxides of molybdenum and vanadium is greater than that of the other three. Alumina has a slight activity, which is probably that of a dehydrating catalyst, as water is one of the products of the reaction. Commercial tellurium and the oxides of calcium, barium, and silicon have no appreciable activity. In the case of iron and antimony, a part of the reduction is due to the direct action of the metal, an oxide being formed. When antimony is used at a low temperature, the catalyst loses its activity, which is restored by heating at 450° in hydrogen. When, however, antimony is used at 320° it does not lose its activity with use. J. F. S.

Migration of the Methyl Residue into the Benzene Nucleus. The Transformation of Methylaniline Hydrochloride into Toluidine Hydrochloride. ERNST BECKMANN and ERICH CORRENS [with OTTO LIESCHE] (*Ber.*, 1922, 55, [B], 852–856).—The conversion of methylaniline hydrochloride into toluidine hydrochloride has been regarded as an intramolecular change of the first order due to a direct exchange of position of the methyl group and a hydrogen atom, or, alternatively, as due to the preliminary production of methyl chloride and subsequent action of the latter on the aniline. The proof that a tertiary base is also produced greatly strengthens the latter conception.

Experiments with methylaniline hydrochloride show that the Hofmann-Martius reaction does not take place at 235°; at 260°, a mixture of primary and secondary amines in about equal proportions is produced whereas at 310° the tertiary amine is formed in considerable amount. The course of the reaction does not appear to be influenced to any considerable extent by the presence of aluminium chloride or zinc chloride, the temperature being the fundamental factor.

Methylaniline is not affected by treatment with concentrated

sulphuric acid at 100° or with a saturated solution of hydrogen chloride in glacial acetic acid and acetic anhydride at 150°; the Hofmann-Martius reaction does not therefore appear to be analogous to the Beckmann transformation.

H. W.

2:3- and 2:5-Dinitro-*p*-toluidines. JAMES SCOTT and ROBERT ROBINSON (T., 1922, 121, 844—846).

Complex Tautomerism. H. LEY and R. GRAU (Z. physikal. Chem., 1922, 100, 271—275).—When to a complex compound, formed between a nitrohydrocarbon, $H \cdot R(NO_2)_n$, and an aromatic amine, $R'NA_2$, of the type $HR(NO_2)_n \dots R'NA_2$, a salt-forming group, XH , is added, the hydrogen of which can form an ion, then the resulting compound may exist in two possible forms, $(NO_2)_nRX[H \dots NR'A_2]$ and $HXR(NO_2)_n \dots R'NA_2$. Evidence is advanced to prove that in the case of the complex formed between 3:5-dinitrobenzoic acid and diethylaniline, the two tautomers actually exist. The complex forms light yellow crystals which dissolve in water to form a colourless solution. The solution has a marked electrical conductivity which points to the saline character of the dissolved substance. In chloroform, methyl alcohol, ethyl alcohol, amyl alcohol, and ethyl ether, the solution is yellow to yellowish-red. It melts at 93°, but when heated under water at 73°, brownish-red liquid drops are formed which on solidifying pass back to the white form, which again melts at 93°. J. F. S.

The Catalytic Reduction of Aromatic Nitro-compounds and a New Method for the Preparation of β -Arylhydroxylamines. I. K. BRAND and JOSEPH STEINER (Ber., 1922, 55, [B], 875—887).—Nord (A., 1920, i, 21) has studied the course of the catalytic reduction of nitrobenzene in the presence of a platinum catalyst and has thereby established the intermediate production of β -phenylhydroxylamine; he has, however, been led to the conclusion that the method does not allow ready control, and that the intermediate products are only present in such small amount as to render their isolation and identification a matter of extreme difficulty. It is now found, however, that under suitable conditions β -arylhydroxylamines, azoxy- and hydrazo-derivatives can be prepared in good yield. The compounds first named are obtained in neutral solution, whereby the possibility of the conversion of initially-formed β -arylhydroxylamines into azoxy-compounds, aminophenols, or chloroamines is practically excluded. Reduction is effected by hydrogen at the atmosphere pressure in the presence of palladised animal charcoal, the extent of the action being controlled by regulation of the volume of the hydrogen used; provided that the change does not occur too vigorously, there is little fear of the further reduction of β -arylhydroxylamine to primary amine so long as unchanged nitro-derivative is present. Under these conditions, nitrobenzene yields successively β -phenylhydroxylamine in 80% yield and (with a further supply of hydrogen) aniline in 90% yield. *m*-Dinitrobenzene yields 1-nitro-3-hydroxylaminobenzene [β -*m*-nitrophenylhydroxylamine], m. p. 118—119°

(cf. Brand, A., 1906, i, 80), *m*-nitroaniline, and *m*-phenylenediamine. 2:4-Dinitrotoluene is converted successively into 2-nitro-4-hydroxylaminotoluene (Brand and Zöller, A., 1907, i, 755) and 2:4-tolylenediamine, whereas 2:6-dinitrotoluene gives 2-nitro-6-hydroxylaminotoluene (Brand, A., 1911, i, 713), 2-nitro-6-aminotoluene, m. p. 92°, and 2:6-tolylenediamine.

The smooth formation of azoxy-compounds depends essentially on the alkalinity of the solution, which must be sufficient to promote the rapid production of the desired substance and thus to repress the further reduction of the β -arylhydroxylamine to primary amine. Palladised animal charcoal is used as catalyst. Under these conditions, nitrobenzene is transformed by the requisite quantities of hydrogen into azoxybenzene and hydrazobenzene, whereas with a smaller concentration of alkali hydroxide the main product is aniline, the formation of which is not due to fission of intermediately formed azoxybenzene; in aqueous alcoholic solution, azoxybenzene and azobenzene are converted by the requisite amounts of hydrogen into hydrazobenzene, aniline not being produced in more than minimal quantity. *m*-Dinitrobenzene gives 1:1'-dinitro-3:3'-azoxybenzene, m. p. 146.5° (cf. Brand, A., 1906, i, 80). 2:4- and 2:6-Dinitrotoluenes are transformed respectively into 2:2'-dinitro-4:4'-azoxytoluene, m. p. 164°, and 2:2'-dinitro-6:6'-azoxytoluene, m. p. 188° (cf. Brand and Zöller, A., 1907, i, 755).

H. W.

Semipinacolic Transposition in the Benzylcyclohexene Series; Migration of the Benzene Radicle. M. Tiffeneau and M. Porcher (*Bull. Soc. chim.*, 1922, [iv], 31, 324—334).—1-Benzylcyclo- Δ^1 -hexene, obtained by the dehydration of benzylcyclohexanol, gives, in ethereal solution with mercuric oxide and iodine, 2-iodo-1-benzylcyclohexan-1-ol, which when shaken in ethereal solution with silver nitrate yields a mixture of the original hexene, its oxide, and 1-benzylcyclohexan-2-one, b. p. 165—166°/18 mm., d_4^{20} 1.0733, giving a semicarbazone, m. p. 166—167°. 1-Benzylcyclohexan-2-one may also be prepared from cyclohexanone by the action of sodamide followed by the addition of benzyl chloride. A fourth product of the action of silver nitrate on the iodohydrin is 1-benzylcyclohexan-1:2-diol, m. p. 96—97°, which on dehydration gives benzylcyclohexanone.

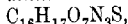
4-Benzyl-1-methylcyclohexan-4-ol, b. p. 183—187°/25 mm., obtained by the action of magnesium benzyl chloride on 1-methylcyclohexan-4-one, on dehydration gives 4-benzyl-1-methylcyclo- Δ^3 -hexene, b. p. 160—165°/35 mm., from which 3-iodo-4-benzyl-1-methylcyclohexan-4-ol can be prepared. This iodohydrin does not give a ketone when shaken in ethereal solution with silver nitrate.

W. G.

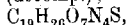
Nitro-derivatives of *p*-Phenetidine. FREDERIC REVERDIN and H. P. ANDRÉ ROETHLISBERGER (*Helv. Chim. Acta*, 1922, 5, 300—314).—The reactivity of the 2-nitro-group in 2:3:5-trinitro-*p*-phenetidine (Reverdin and Fürstenberg, A., 1913, i, 850) is preserved in its *p*-toluenesulphonyl derivative. In 2:3-dinitro-

p-phenetidine, however, it is the 3-nitro-group which exhibits reactivity, and this is enhanced by acylation, the benzoyl being more effective than the acetyl group in this respect. 2:3-Di- and 2:3:5-tri-nitro-*p*-phenetidines are best prepared by nitration of *p*-toluenesulphonyl-*p*-phenetidine (Reverdin and Fürstenberg, *loc. cit.*) or its 3-nitro-derivative (detailed directions for which are supplied), followed by hydrolysis. 2:5-Dinitro-*p*-toluenesulphonyl-*p*-phenetidine, $C_{15}H_{15}O_7N_3S$, prisms or rosettes, m. p. 152–154°, is a subsidiary product in the preparation of the 2:3-isomeric. The orientation of 2:5-dinitro-*p*-phenetidine, $C_8H_9O_5N_3$, scarlet needles, m. p. 139–139.5° (acetyl derivative, $C_{10}H_{11}O_6N_3$, yellow needles, m. p. 156–157°), follows from its conversion into 2:5-dinitrophenetole, m. p. 96–98° (cf. Andreae, A., 1880, 466), from which 2:5-dinitrophenol is obtained by means of concentrated sulphuric acid at 60–70°. Similarly, 2:5-dinitro-4-aminophenol, $C_8H_9O_5N_3$, violet-black needles, m. p. 166–167°, is produced from 2:5-dinitro-*p*-phenetidine, although the corresponding anisidine is stable under these conditions. 2:5-Dinitro-4-aminophenyl acetate, $C_8H_9O_6N_3$, m. p. 144–145°, exists in a yellow and a red form. Chromoisomerism is also exhibited by 3-nitro-*p*-toluenesulphonyl-*p*-phenetidine (large, pale yellow, cubic crystals, m. p. 104–105°; intensely yellow, fine needles, m. p. 94–95°), 2:3-dinitrotoluenesulphonyl-*p*-phenetidine (fine, pale yellow needles, m. p. 143–146°; almost colourless, cubic crystals, m. p. 162–163°; cf. Reverdin and Fürstenberg, *loc. cit.*).

p-Toluenesulphonyl-2:3-dinitro-*N*-methyl-*p*-phenetidine,



forms needles, or tablets, m. p. 152–152.5°. Benzoyl-2:3-dinitro-*p*-phenetidine, forms pale yellow plates, m. p. 182–183°. Benzoyl-2:3:5-trinitro-*p*-phenetidine, $C_{15}H_{13}O_8N_4$, forms pale yellow needles, m. p. 246–247° (decomp.). *p*-Toluenesulphonyl-2-nitro-3-anilino-*p*-phenetidine, $C_{21}H_{22}O_7N_4S$, crystallises in ruby-red needles, m. p. 111–111.5°. Acetyl-2-nitro-3-anilino-*p*-phenetidine, $C_{16}H_{17}O_4N_3$, brown plates, m. p. 151–152°; the benzoyl analogue, $C_{21}H_{19}O_4N_3$, dark brown crystals, m. p. 153–154°, furnishes benzoyl-2-nitro-3-methylamino-*p*-phenetidine, $C_{16}H_{17}O_4N_3$, dark brown crystals, m. p. 135–136°. *p*-Toluenesulphonyl-3:5-dinitro-2-anilino-*p*-phenetidine, $C_{21}H_{20}O_7N_4S$, forms yellow prisms, m. p. 198–199°. 3:5-Dinitro-2-methoxy-*p*-phenetidine, $C_9H_{11}O_6N_3$, forms orange needles, m. p. 120–121°. The following molecular compounds are described: *p*-Toluenesulphonyl-2:3-dinitro-*p*-phenetidine with methylamine, $C_{16}H_{20}O_7N_4S$, m. p. 148–149°; with dimethylamine, $C_{17}H_{22}O_7N_4S$, red crystals, m. p. 141°; with ethylamine, $C_{17}H_{22}O_7N_4S$, orange needles, m. p. 146° (decomp.); with diethylamine,



red or yellow plates, m. p. 182–183°; with aniline, $C_{21}H_{22}O_7N_4S$, plates, m. p. 141–142°; with quinoline, $C_{24}H_{22}O_7N_4S$, yellow cubic crystals, m. p. 94–96°, and a potassium salt, $C_{25}H_{14}O_7N_4SK$, orange-yellow needles, m. p. 296–297°. *p*-Toluenesulphonyl-2:3:5-trinitro-*p*-phenetidine, gives with dimethylamine, $C_{17}H_{21}O_8N_4S$,

red form, m. p. 164° , and an orange form, m. p. 184° ; with *tri-nethylamine*, $C_{18}H_{28}O_9N_3S$, canary yellow needles, m. p. $175-176^{\circ}$ (decomp.); and with *quinoline*, $C_{24}H_{21}O_9N_3S$, orange red needles, m. p. $102-103^{\circ}$ (decomp.). *p-Toluenesulphonyl-3-nitro-p-phenetidine* forms with *diethylamine*, $C_{19}H_{27}O_5N_3S$, red needles, m. p. $135-136^{\circ}$. *p-Toluenesulphonyl-2:5-dinitro-p-phenetidine*, gives with *dimethylamine*, $C_{17}H_{22}O_7N_4S$, red or yellow plates, m. p. $178-179^{\circ}$. J. K.

Action of Nitric Acid on Phenol Ethers. KURT H. MEYER and HANS GOTTLIEB-BILLROTH (*Ber.*, 1922, 55, [B], 823-826; cf. A., 1920, i, 37).—A reply to Kehrman, Decker, and Solonina (this vol., i, 32). H. W.

The Oxidation of Quinol in the Presence of Aliphatic Amines. ROLLA N. HARGER (*Proc. Nat. Acad. Sci.*, 1922, 8, 57-59).—Quinol, dissolved in a strong aqueous solution of dimethylamine, takes up oxygen readily, and brilliant, red plates separate, m. p. 171° , which appear to be 2:5-di-dimethylaminoquinol (cf. Mylius, A., 1885, i, 803; Kehrman, A., 1890, i, 756). Other products not yet identified are also formed in the reaction. Similar results have been obtained with methylamine. W. O. K.

The Iodohydrin Derived from Allylbenzene and its Transformations. M. PORCHER (*Bull. Soc. chim.*, 1922, [iv], 31, 334-340).—Allylbenzene gives with mercuric oxide and iodine in moist ether α -*iodo- γ -phenylpropan-3-ol*, which under the influence of silver nitrate yields benzyl methyl ketone together with some allylbenzene oxide and some benzylethylene glycol as its nitrate. Allylbenzene oxide reacts with hydriodic acid to give a mixture of the above iodohydrin and its isomeride, β -*iodo- γ -phenylpropan-2-ol*, and if this mixture is treated with silver nitrate, phenylpropaldehyde is obtained in addition to benzyl methyl ketone.

Allylbenzene dibromide gives with alcoholic potassium hydroxide *benzylvinyl bromide*, $CH_2Ph\cdot CH:CHBr$, b. p. $217-221^{\circ}$, d_4^{20} 1.351. This reacts with magnesium in ethereal solution, giving phenylpropinene (cf. Lespieau and Garreau, A., 1920, i, 603), allylbenzene, and magnesium derivatives of these two hydrocarbons. W. G.

Halochromic Phenomena with Carbinols. SIEGFRIED SKRAUP and LEO FREUNDLICH (*Ber.*, 1922, 55, [B], 1073-1080).—A preliminary communication induced by the recent publications of Hess and Weltzein (this vol., i, 35) and Ziegler (this vol., i, 151).

The basic character of carbinols is regarded as a consequence of the great valency demand on the central carbon atom. If this is the case, the hydroxyl of a carbinol must be the more readily removable from the central carbon atom by complex- or salt-forming agents (that is, the resulting halochromic salt must be the less sensitive towards hydrolysing agents) in proportion as the substituents make greater demands on the valency of the central carbon atom. It follows, therefore, that, in the presence of a suitable radicle, one or two phenyl residues in triphenylcarbinol can be replaced even by aliphatic groups without causing the disappear-

ance of halochromism, and ultimately that even primary and secondary alcohols may be halochromic. An intimate connexion exists between the halochromism and basicity of the carbinols and the radicle dissociation of the corresponding hexa-alkylethanes to substituted methyls; this is illustrated by a number of instances. The basicity of the carbinols is measured by treating their solutions in glacial acetic acid with a solution of concentrated sulphuric acid in the same solvent and titrating with alcohol (75%) until the colour is discharged. It is interesting to note that the method can be extended to benzoic acid and its esters, although in these cases the initial coloration, for some unexplained reason, is only developed when undiluted sulphuric acid is added to the solutions. The following series of basicities is recorded, that of triphenylcarbinol being adopted as unit in each series: (1) diphenyl-*p*-tolylcarbinol, 2.55; diphenyldiphenylcarbinol, 3.19; diphenyl-*p*-anisylcarbinol, 6.99; α -naphthyldiphenylcarbinol, 8.83; (2) benzhydrol, 0.330; diphenylmethylcarbinol, 0.361; diphenylethylcarbinol, 0.343; diphenylpropylcarbinol, 0.368; *p*-anisyl dimethylcarbinol, 0.972; (3) benzoic acid, 0.806; methyl benzoate, 0.501; ethyl benzoate, 0.429.

The following substances are described incidentally: *diphenylpropylcarbinol*, m. p. 36°; *p*-anisyl dimethylcarbinol, b. p. 130°/high vacuum; *triisobutylcarbinol*, which could not be isolated in the homogeneous state. H. W.

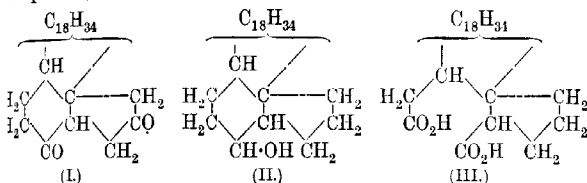
Carboligase. IV. CARL NEUBERG and HEINZ OHLE (*Biochem. Z.*, 1922, 128, 610—618).—Improved experimental methods have confirmed and amplified the previous work (A., 1921, i, 480; this vol., i, 305) on the production of *l*-acetylphenylcarbinol from benzaldehyde during yeast fermentation. The *senicarbazon* of *l*-acetylphenylcarbinol has m. p. 194° and $[\alpha]_D^{25} + 215.78^\circ$ in pyridine. The *thiosemicarbazon* has now been obtained optically active by combination of the components in pyridine solution. It melts at 207° and has $[\alpha]_D^{25} + 228.78$ in pyridine. The formation of the thiosemicarbazon can be used for estimating the approximate content of the ketone-alcohol in the crude oil (ether extract). The value found was 27%. In the fractionation of the ketone-alcohol fraction, phenyldiketopropane was identified by its oxime and phenylhydrazon. H. K.

Diphenylstyrylcarbinol and Triphenylallene. KURT H. MEYER and KURT SCHUSTER (*Ber.*, 1922, 55, [B], 815—819). *Diphenylstyrylcarbinol*, $\text{CHPh}:\text{CH}:\text{CPh}_2\cdot\text{OH}$, colourless needles, m. p. 95°, is prepared in 14% yield by the action of magnesium β -styryl bromide on benzophenone in ethereal solution (cf. Ziegler, this vol., i, 151). Attempts to convert it into the corresponding chloride (and hence to an analogue of triphenylmethyl in which one phenyl group is replaced by an unsaturated residue) were unsuccessful, since it is transformed by acetyl chloride, acetic anhydride, or a solution of hydrogen chloride in ether into *triphenylallene*, $\text{CHPh}:\text{C}:\text{CPh}_2$, colourless, lustrous leaflets, m. p. 210°.

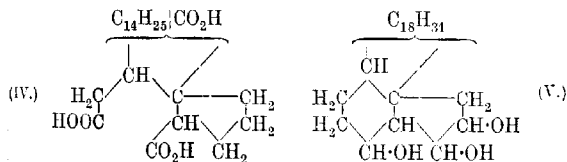
The preparation of the carbinol, $\text{CPh}_2\cdot\text{CPh}\cdot\text{CPh}_2\cdot\text{OH}$, could not be effected, since methyl triphenylacrylate could not be caused to react with magnesium phenyl bromide, even when dissolved in boiling *cyclohexyl methyl ether*.

II. W.

Cholesterol. A. WINDAUS (*Z. physiol. Chem.*, 1921, **117**, 146–158; cf. *A.*, 1920, i, **41**, 309, 434, 435; 1921, i, 507).—I. [With HARRY GRIMMEL.]—The ketodicarboxylic acid, $\text{C}_{27}\text{H}_{44}\text{O}_5$, formed by the oxidation of cholestan-4:7-dione (I) forms a *semi-carbazide* (slender needles, m. p. 240°) which with sodium ethoxide and alcohol yields an acid, $\text{C}_{27}\text{H}_{46}\text{O}_4$, identical with an acid obtained by the oxidation of dihydrocholesterol (II); it therefore has the constitution (III). This is confirmed by the fact that when heated, it forms a *diketone*, $\text{C}_{26}\text{H}_{42}\text{O}_2$, small plates, m. p. $148\text{--}149^\circ$ (*dioxime*, m. p. 191°).



II. [With A. VON STADEN.]—From the dicarboxylic acid, $\text{C}_{27}\text{H}_{46}\text{O}_4$ (III), a *tricarboxylic acid*, $\text{C}_{24}\text{H}_{38}\text{O}_6$ has been prepared by oxidation with chromic acid, which crystallises from acetic acid in rosettes of slender needles, m. p. 238° , and forms a *trimethyl ester*, rectangular leaflets, m. p. $86\text{--}87^\circ$. This acid apparently has the constitution (IV.)



III. [With H. LÜDERS.]—On boiling α -cholestan-triol (V) (T., 1908, **93**, 1680; *A.*, 1915, i, 884) with methyl alcoholic hydrogen chloride, it is converted into the *chlorohydrin* of α -cholesterol oxide, $\text{C}_{27}\text{H}_{44}\text{O}_2\text{Cl}$, long needles, m. p. $170\text{--}171^\circ$. With alcoholic potassium hydroxide, or with acid, β -cholesterol oxide is obtained, identical with that isolated by Westphalen (*A.*, 1915, i, 885).

W. O. K.

Metacholesterol and its By-products. III. I. LIFSCHÜTZ (*Biochem. Z.*, 1922, **129**, 115–127).—The author amplifies the description of the properties and preparation of metacholesterol (*A.*, 1920, i, 546). It has mol. wt. 369 and $[\alpha]_D -33.7^\circ$ in chloroform.

H. K.

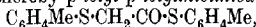
Derivatives of Dithioethylene and Dithioacetylene and the Additive Capacity of Multiple Bonds. EMIL FROMM and ERICH SIEBERT (*Ber.*, 1922, 55, [B], 1014—1030).—The additive capacity of the double and treble linking in di-*p*-tolylthioethylene and di-*p*-tolylthiolacetylene is suppressed completely towards hydrogen and partly towards bromine; addition of the elements of water is, however, possible. The substances can also be oxidised, but the oxygen atoms become attached to sulphur. Since the activity of the multiple bond is lessened by the proximity of mercaptan residues, it would be expected that a still more marked effect would be produced by neighbouring sulphonyl radicles. This is actually the case with respect to the addition of bromine, but, on the other hand, the sulphonyl compounds are readily reduced by hydrogen; the apparent anomaly is explained by the observation of the presence of conjugated double bonds, whereby also the behaviour of the sulphones towards phenylhydrazine is explained.

Di-p-tolylthioethylene, $C_6H_5(S \cdot C_6H_4Me)_2$, long, lustrous needles, m. p. 93° , is prepared in 90% yield by the gradual addition of $\alpha\beta$ -dichloroethylene to a boiling alcoholic solution of *p*-tolyl mercaptan and potassium hydroxide. When dissolved in chloroform, it is converted by bromine into the corresponding dibromide, $C_2H_2Br_2(S \cdot C_6H_4Me)_2$, a somewhat unstable, colourless, crystalline powder, m. p. 72° , and by chlorine into the dichloride, m. p. 138° . The dibromide is transformed by boiling alcoholic potassium hydroxide solution into *di-p-tolylthiolacetylene*, long, lustrous needles, m. p. 101 – 102° , which combines with bromine in chloroform solution to give *di-p-tolylthiolacetylene dibromide*, $C_2Br_2(S \cdot C_6H_4Me)_2$, m. p. 99 – 100° ; the latter substance does not unite further with bromine. *Di-p-tolylthioethylene* is prepared by the action of zinc dust and boiling glacial acetic acid on *di-p-tolylthioethylene dibromide* or *di-p-tolylthiolacetylene dibromide*. *Di-p-tolylthioethylene* is converted by sulphuric acid (50%) in glacial acetic acid solution into the *p-tolylmercaptal* of *p-tolylthiolacetaldehyde*, $C_6H_4Me \cdot S \cdot CH_2 \cdot CH(S \cdot C_6H_4Me)_2$, colourless, unctuous leaflets, m. p. 62 – 63° . The course of the reaction is probably represented by the schemes: $C_6H_4Me \cdot S \cdot CH_2 \cdot CH \cdot S \cdot C_6H_4Me \rightarrow C_6H_4Me \cdot S \cdot CH_2 \cdot CH(OH) \cdot S \cdot C_6H_4Me \rightarrow C_6H_4Me \cdot S \cdot CH_2 \cdot CHO + 2SH \cdot C_6H_4Me = C_6H_4Me \cdot S \cdot CH_2 \cdot CH(S \cdot C_6H_4Me)_2 + H_2O$; this view is supported by the observation that the yield of the product is increased when the reaction takes place in the presence of added *p*-tolyl mercaptan. Oxidation of the *p-tolylmercaptal* with potassium permanganate leads to the production of the *p-tolylsulphonosulphidemercaptal* of *p-toluenesulphonylacetaldehyde*,

$C_6H_4Me \cdot SO_2 \cdot CH_2 \cdot CH(S \cdot C_6H_4Me) \cdot SO_2 \cdot C_6H_4Me$, slender, colourless needles, m. p. 119 – 120° , which is reduced by zinc dust in boiling glacial acetic acid solution to *di-p-toluenesulphonylethane*, $C_2H_4(SO_2 \cdot C_6H_4Me)_2$, m. p. 199 – 200° . If, however, the mercaptal is oxidised with hydrogen peroxide (30%), it is converted into the *p-tolylsulphonmercaptal* of *p-toluenesulphonyl-*

acetaldehyde, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CH}(\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me})_2$, colourless needles, m. p. $222-223^\circ$, which is also reducible by zinc and acetic acid to di-*p*-toluenesulphonylethane.

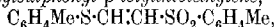
Di-*p*-tolylthiolacetylene likewise unites with the elements of water when treated with sulphuric acid in glacial acetic acid solution, yielding thereby *p*-tolyl *p*-tolylthiothioacetate,



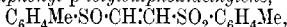
a liquid which could neither be caused to crystallise, nor distilled without decomposition; it is hydrolysed to *p*-tolyl mercaptan and *p*-tolylthiolacetic acid, m. p. 93° , which is readily oxidised to *p*-tolylsulphonylacetic acid, m. p. $117.5-118.5^\circ$.

Di-*p*-tolylthioethylene is not attacked by zinc dust and acetic acid, but is converted by sodium and alcohol into *p*-tolyl mercaptan.

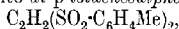
Oxidation of di-*p*-tolylthioethylene dissolved in benzene with potassium permanganate and dilute sulphuric acid leads to the formation of *p*-tolylsulphonyl-*p*-tolylthioethylene,



lustrous needles, m. p. $114-115^\circ$; the constitution of the substance is deduced from its reduction by zinc dust and glacial acetic acid to *p*-toluenesulphonyl-*p*-tolylthioethane, slender, colourless needles, m. p. $117-118^\circ$, and oxidation of the latter to di-*p*-tolylsulphonylethane, m. p. $199-200^\circ$. Oxidation of di-*p*-tolylthioethylene dissolved in cold acetic acid with hydrogen peroxide (30%) gives *p*-toluenesulphonyl-*p*-tolylsulphoxidethylene,

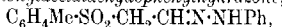


m. p. $122-123^\circ$, which, like other sulphoxides, gives a yellow coloration with alkali hydroxide and loses an oxygen atom when reduced, thus yielding *p*-toluenesulphonyl-*p*-tolylthioethane. Oxidation with hydrogen peroxide (30%) in warm solution transforms the dithio-compound into di-*p*-toluenesulphonylethylene,



long, lustrous needles, m. p. $149-150^\circ$, which is reduced by nascent hydrogen to di-*p*-tolylsulphonylethane.

Di-*p*-toluenesulphonylethylene is converted by phenylhydrazine in alcoholic solution at the atmospheric temperature into the phenylhydrazine salt of toluene-*p*-sulphinic acid, m. p. $159-160^\circ$, and *p*-toluenesulphonylacetaldehydephenylhydrazone,



yellow needles, m. p. $144-145^\circ$. A similar change occurs with the sulphoxidesulphone, the products being *p*-toluenesulphonylacetaldehydephenylhydrazone and *p*-tolyl disulphide. H. W.

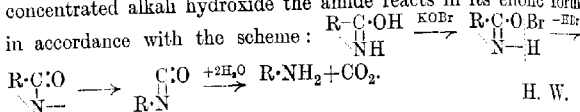
Interchange of Alcohol Radicles in Esters. AKIRA SHIMOMURA and JULIUS BEREND COHEN (T., 1922, 121, 883-887).

Preparation of Aromatic Esters in the Presence of an Organic Base. YOSHITARÔ SUZUKI and SANKYÔ KABUSHIKI KAJIHA (Japanese Pat. 38647 [1921]).—Aromatic esters are easily prepared from aromatic alcohols and chlorides or bromides of aromatic acids in the presence of an organic base, such as pyridine.

As an example, benzyl benzoate is prepared by dropping 400 parts of benzoyl chloride into a mixture of 300 parts of benzyl alcohol and 300 parts of pyridine at 50°. After mixing, the liquid is warmed on a water-bath for three to four hours, freed from the base and acid by washing with warm water and alkali, and then rectified. Benzyl cinnamate, benzyl nitrobenzoate, and benzyl bromobenzoate are also prepared by the same method.

K. K.

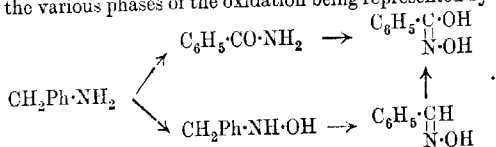
Hofmann's Degradation of Acid Amides to Amines. ERNST BECKMANN and ERICH CORRENS [with OTTO LIESCHER] (*Ber.*, 1922, 55, [B], 848—851).—*m*-Bromobenzamide is converted by bromine and potassium hydroxide solution into *m*-bromoaniline, whilst *p*-bromobenzamide yields *p*-bromoaniline, the substituent therefore occupying the same position after as before the intramolecular transformation (cf. Montagne, A., 1918, i, 534). It therefore appears that the displacement of the radicle occurs in the same manner in the Hofmann degradation as in the Beckmann transformation. It is possible that in the presence of the concentrated alkali hydroxide the amide reacts in its enolic form in accordance with the scheme:



H. W.

Action of Hydrogen Peroxide on Nitriles and on Amides: Formation of Hydroxamic Acids. E. OLIVERI-MANDALA (*Gazzetta*, 1922, 52, i, 107—112).—In alkaline solution at about 40°, hydrogen peroxide converts nitriles into the corresponding amides (cf. Radziszewski, A., 1885, 496; Deinert, A., 1896, i, 149; Dubsky, A., 1916, i, 550). The author finds that, with perhydrol in faintly alkaline solution, this hydrolysis proceeds further, ammonia and the acid corresponding with the nitrile being obtained: $\text{R}-\text{CN} + 3\text{H}_2\text{O}_2 = \text{R}-\text{CO}_2\text{H} + \text{NH}_3 + \text{H}_2\text{O} + 3\text{O}$. If an aromatic nitrile is used and the solution contains also a little ferric chloride, the cherry-red coloration characteristic of the hydroxamic acids gradually appears. Hydroxamic acids are formed also from aromatic amides under these conditions, the ferric chloride exerting a catalytic influence on the reaction.

In the oxidation of benzylamine to benzaldoxime by means of Caro's acid, $\text{CH}_2\text{Ph}\cdot\text{NH}_2 \rightarrow \text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{OH} \rightarrow \text{CHPh}\cdot\text{NOH}$, it is not improbable that the hydroxamic acid forms an intermediate stage, the various phases of the oxidation being represented by the scheme:



The action of diazomethane on benzhydroxamic acid in ethereal solution yields a compound, $\text{C}_8\text{H}_9\text{O}_2\text{N}$, with properties identical

with those of the compound obtained by Lossen by the action of potassium hydroxide and methyl iodide on benzhydroxamic acid (A., 1895, i, 37) and regarded by this author as having the oximic structure, $\text{OH}\cdot\text{CPh}\cdot\text{N}\cdot\text{OMe}$. Since, however, ethers are known in which both hydroxyls are undoubtedly etherified, for instance, $\text{OR}\cdot\text{CPh}\cdot\text{N}\cdot\text{OR}$, and since also diazomethane is capable of etherifying feebly acid hydrogen atoms, such as the hydroxylic hydrogen atoms of phloroglucinol, Lossen's formula for the above compound is to be excluded, the true structure being either $\text{COPh}\cdot\text{NH}\cdot\text{OMe}$ or $\text{O} < \begin{smallmatrix} \text{N}\cdot\text{OR} \\ \text{CPh} \end{smallmatrix}$. The salts of compounds of this class have, however, probably the oximic constitution.

T. H. P.

Free *o*-Aminophenylacetic Acid, its Esters and Transformations. P. W. NEBER (*Ber.*, 1922, 55, [B], 826–848).—The readiness with which *o*-aminophenylacetic acid passes by loss of water into oxindole has caused it to be regarded as a particularly unstable substance which cannot exist in the free state. It is shown, however, that this change is characteristic of solutions acidified with mineral acid; the substance can be isolated readily by the reduction of *o*-nitrophenylacetic acid in alkaline solution and behaves as a normally stable compound.

Barium *o*-aminophenylacetate is prepared readily by the addition of a hot, aqueous solution of barium hydroxide to a mixture of barium *o*-nitrophenylacetate and ferrous sulphate dissolved in hot water; the sodium salt ($+3\text{H}_2\text{O}$), *silver* salt, slender needles, and *copper* salt are described. The free *acid*, colourless, highly refractive needles, m. p. 119° (decomp.), is almost quantitatively precipitated by the addition of a slight deficiency of sulphuric acid to an aqueous solution of the sodium salt. The following derivatives are described: *o*-acetylaminophenylacetic acid (from the acid and acetic anhydride in the presence of ice and water), colourless crystals, m. p. 158° (when heated rapidly) after softening at 150° ; *o*-benzoylaminophenylacetic acid (from barium *o*-aminophenylacetate, aqueous sodium hydroxide, and benzoyl chloride), colourless needles, m. p. 179° after softening at 170° ; *methyl o*-benzoylaminophenylacetate (from the free acid and methyl sulphate), small colourless needles, m. p. 108° . *o*-Aminophenylacetic acid can be diazotised by the gradual addition of sulphuric acid to its aqueous solution in the presence of sodium nitrite; the diazonium compound couples with β -naphthol, giving *o*-3-naphtholazo-phenylacetic acid, $\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_2$, red needles, m. p. 211 – 213° (the sodium salt is described). *o*-Nitrobenzylidene-*o*-aminophenylacetic acid, colourless needles, m. p. 146° after softening at 142° , is prepared from the acid and *o*-nitrobenzaldehyde in boiling alcoholic solution; the corresponding *m*-nitrobenzylidene compound, yellow needles, m. p. 147° , and *p*-nitrobenzylidene derivative, yellow needles, m. p. 137° , are prepared similarly. When heated together at 115° , *o*-nitrobenzaldehyde and *o*-aminophenylacetic acid give 3-*keto*-2-*o*-nitrophenyl-3:4-dihydroquinoline (or 3-hydroxy-2-*o*-nitrophenyl-

quinoline), yellowish-red needles, m. p. 227°. *Phenylacetic-o-sulphinic anhydride*, $\text{C}_6\text{H}_4\text{CH}_2\text{SO}_2\text{CO}$, colourless crystals, m. p. 183°

after softening at 177°, is prepared by the successive treatment of diazotised *o*-aminophenylacetic acid with sulphur dioxide and copper bronze. Reduction of the diazonium solution with stannous chloride and concentrated hydrochloric acid gives *o*-hydrazino-phenylacetic acid, colourless needles ($? + \text{H}_2\text{O}$), m. p. 121°; this substance is converted by rapid distillation under atmospheric pressure into 1-amino-oxindole, $\text{C}_6\text{H}_4\text{CH}_2\text{N}(\text{NH}_2)\text{CO}$, colourless, lustrous leaflets, which is transformed by nitrous acid successively into oxindole and β -isatoxime, m. p. 220° (decomp.). *o*-Nitrobenzylidenearmino-oxindole, yellow needles, m. p. 170° after softening at 163°, is prepared by the addition of *o*-nitrobenzaldehyde to a hot solution of *o*-hydrazinophenylacetic acid in acetic acid and water.

Somewhat unexpectedly, *o*-aminophenylacetic acid can be esterified by saturating a well-cooled solution of it in the requisite alcohol with hydrogen chloride. In this manner, *ethyl o*-aminophenylacetate is prepared as a pale red liquid which could not be caused to crystallise and decomposes with formation of oxindole when distilled under diminished pressure. It is transformed by acetic anhydride into *ethyl o*-acetylaminophenylacetate, colourless needles, m. p. 66°; *o*-acetylaminophenylacetamide crystallises in colourless needles, m. p. 203°. *Ethyl o*-benzoylaminophenylacetate, needles, m. p. 82°, is prepared from the amino-ester and benzoyl chloride in the presence of pyridine. Diazotisation of *ethyl o*-aminophenylacetate and subsequent coupling with β -naphthol yields *ethyl o*- β -naphtholazophenylacetate, red needles, m. p. 127°, which can also be prepared by esterification of the corresponding acid. The amino-ester is converted by *o*-nitrobenzaldehyde in boiling alcoholic solution in the presence of piperidine into *ethyl o*-nitrobenzylidene-*o*-aminophenylacetate, m. p. 58°; the corresponding *m*-nitrobenzylidene compound, pale yellow needles, m. p. 119°, and *p*-nitrobenzylidene derivative, yellow crystals, m. p. 125°, are also described.

Methyl o-aminophenylacetate is obtained as a liquid which could neither be caused to crystallise nor be distilled without decomposition. The following derivatives are described: *methyl o*-acetylaminophenylacetate, a colourless powder, m. p. 90° after softening at 87°; *o*-acetylaminophenylacetamide, m. p. 203°; *methyl o*-benzoylaminophenylacetate, colourless slender needles, m. p. 108°; *methyl o*-nitrobenzylidene-*o*-aminophenylacetate, pale yellow needles, m. p. 79°; *methyl m'*-nitrobenzylidene-*o*-aminophenylacetate, yellow needles m. p. 97° after softening at 91°; *methyl p'*-nitrobenzylidene-*o*-aminophenylacetate, yellow needles, m. p. 107° after softening at 105°; *methyl o*- β -naphtholazophenylacetate, brilliant red needles m. p. 145°.

o-Azoxyphenylacetic acid, m. p. 250°, is obtained in small amount

varying amount (up to 2%) by the reduction of *o*-nitrophenyl-acetic acid by ferrous sulphate and barium hydroxide. The corresponding *ethyl* ester, pale reddish-yellow needles, m. p. 69°, and *methyl* ester, yellowish-red needles, m. p. 114°, after previous softening, are described; they are very sensitive towards light.

H. W.

Higher Terpene Compounds. II. Abietic Acid. L. RUZICKA and JULES MEYER (*Helv. Chim. Acta*, 1922, 5, 315—344; cf. A., 1921, i, 573).—Abietic acid, as it actually exists in American colophony, is best isolated in a 50% yield by distillation of this material at 200—210°/1 mm. (bath 255°), followed by crystallisation from methyl alcohol or acetone. It forms triangular leaflets, m. p. 158° when rapidly heated, $[\alpha]_D^{20}$ -68.5°; (*triozonide*, $C_{20}H_{30}O_2 \cdot O_3$, m. p. 91—93°, *methyl* ester, $C_{21}H_{32}O_2$, b. p. 168—172°/0.5 mm., d_4^{20} 1.049, n_D^{20} 1.5346). The acid at once decolorises alkaline permanganate and on catalytic reduction in alcoholic solution yields a mixture of presumably two *dihydro-acids*, of which one, $C_{20}H_{32}O_2$, m. p. 167—168°, $[\alpha]_D^{20}$ -12°, was isolated in the pure condition. This acid furnished a *diozonide*, $C_{20}H_{32}O_2 \cdot O_3$, m. p. 97—102° (decomp.), but was indifferent to alkaline permanganate (cf. Virtanen, A., 1920, i, 832), whilst the action of hydrogen bromide in glacial acetic acid solution yielded an *isomeride*, $C_{20}H_{32}O_2$, m. p. 130—131°, $[\alpha]_D^{20}$ about -2°, which is distinguished from all other isomerisation or reduction products of abietic acid by its sparing solubility in alcohol. It is stable towards alkaline permanganate, reacts with difficulty with ozone, the product, m. p. 112—116°, corresponding with the formula $C_{20}H_{32}O_2 \cdot O$. Catalytic reduction of abietic acid in ethyl acetate solution at the ordinary temperature, and more especially in amyl ether at 80°, resulted in the formation of notable quantities of the tetrahydro-acid, $C_{20}H_{34}O_2$, m. p. 167—169°, $[\alpha]_D^{20}$ +10°, the formation of which was complete in glacial acetic acid solution at 80°. This acid reacts with ozone with difficulty, forming somewhat indefinite products, for an account of which the original should be consulted.

The variation in the accounts of abietic acid given by earlier workers is due to the fact that, whilst in some cases [Mach, A., 1893, i, 582; 1895, i, 384; Maly (1861); Flückiger (1867); Tschirch and Studer, A., 1904, i, 79] the extraction of the acid was carried out by means of alcohol or weak alkali, and the products approximately agreed in melting point with that now described, in other instances (Levy, A., 1906, i, 870; Johansson, *Mon. sci.*, 1921, 73) methods were employed which caused isomerisation. This occurs to some extent if the distillation above described be carried out under 2 mm. pressure (bath temperature 275°); if the material is first heated for several hours at 290°, and subsequently distilled under 12 mm. pressure (bath 300°) the main product is an *isomeride*, $C_{20}H_{30}O_2$, m. p. 178—179°, $[\alpha]_D^{20}$ +3°, which yields a mixture of tetrahydro-acids. One of these, $C_{20}H_{34}O_2$, m. p. 169—171°, $[\alpha]_D^{20}$ +3°, has been definitely separated. When abietic acid was heated for

twenty-four hours at 300° in a stream of carbon dioxide and subsequently distilled, a considerable quantity of abietene, b. p. 180—170°/0.5 mm., accompanied the *isomerised acid*, b. p. 200—210°/0.5 mm., m. p. 170—172°, $[\alpha]_D^{20} + 46^\circ$. The last furnished a mixture of di- and tri-ozonides, and a *tetrahydro-acid*, $C_{20}H_{34}O_2$, m. p. 116—118°, $[\alpha]_D^{20} + 16^\circ$, from which what seemed to be a *monozonide of a peroxide*, $C_{20}H_{34}O_2 \cdot O_3$, m. p. 103—106° (decomp.), was prepared. Abietic acid is quite stable towards boiling alcoholic sodium hydroxide solution, and is practically unchanged by glacial acetic acid, or after short treatment with alcoholic hydrogen chloride. After prolonged treatment with a hot solution of hydrogen chloride in glacial acetic acid, however, it melted at 176—177°, $[\alpha]_D^{20} - 34^\circ$, and furnished a *diozonide*, $C_{20}H_{30}O_2 \cdot O_3$, m. p. 71° (decomp.), a *dihydro-acid*, $C_{20}H_{32}O_2$, m. p. 148—149°, $[\alpha]_D^{20} + 27^\circ$ (from which a mixture of mono- and di-ozonides was obtained), and a *tetrahydro-acid*, $C_{20}H_{34}O_2$, m. p. 158—160°, $[\alpha]_D^{20} + 9^\circ$. A further *isomeride* of abietic acid, $C_{20}H_{30}O_2$, m. p. 150—151°, $[\alpha]_D^{20} - 10^\circ$, is obtained by heating its dihydrobromide, m. p. about 178° (cf. Levy, A., 1913, i, 620; Henze, A., 1916, i, 826) with quinoline at 240°. Since abietic acid is a methyldecahydrotetrenecarboxylic acid (Bamberger and Hooker, *Annalen*, 1885, 229, 102; Fortner, A., 1904, i, 739; Lux, A., 1908, i, 873; Bucher, A., 1910, i, 239; Vesterberg, A., 1904, i, 151), and a considerable group of the sesquiterpenes is derived from 1:6-dimethyl-4-isopropyl-naphthalene (see this vol., i, 560), abietic acid would seem to represent the extension of the sesquiterpene compounds in the higher natural series of terpenes.

J. K.

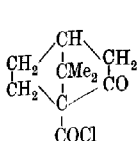
The Action of Potassium Iodide and Iodate on some Hydroxy-acids. SRI KRISHNA and FRANK GEORGE POPE (T, 1922, 121, 798—800).

Neutral Homocamphoric Esters and their Products of Reduction. PALFRAY (*Compt. rend.*, 1922, 174, 1235—1238).—

Ethyl hydrogen camphorate gives an acid chloride, which reacts with sodium phenoxide, giving *phenyl ethyl homocamphorate*, m. p. 51—51.5°, $[\alpha]_D^{20} + 27^\circ 35'$. This ester, on reduction with sodium and absolute alcohol, yields *homocamphoric glycol*, m. p. 63—63.5°, $[\alpha]_D^{20} + 81^\circ 5'$, together with some *hydroxycampholic acid*, $C_8H_{14} \begin{smallmatrix} < CH_2 \cdot CH_2 \cdot OH \\ < CO_2H \end{smallmatrix}$, m. p. 130—131°, $[\alpha]_D^{20} + 71^\circ 37'$. The glycol gives a *diphenylurethane*, m. p. 115—115.5°, $[\alpha]_D^{20} + 31^\circ 29'$; a *diacetyl* derivative, b. p. 182—183°/13 mm., $[\alpha]_D^{20} + 52^\circ 36'$; and a *dibenzoyl* derivative, b. p. 276—277°/2 mm., 295—300°/12 mm., $[\alpha]_D^{20} + 34^\circ 41'$.

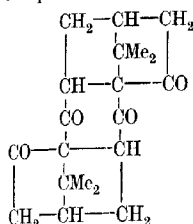
W. G.

Condensation Products from Acid Haloids. X. Action of Triethylamine on Ketopinyl Chloride. E. WEDEKIND and CL. WEINAND (*Ber.*, 1922, 55, [B], 945—951; cf. this vol., i, 234). The "tertiary base" reaction has now been applied to the chloride of a ketonic acid.



Ketopinyl chloride (annexed formula), m. p. 109°, is readily prepared by the action of thionyl chloride on ketopinic acid (cf. Gilles and Renwick, T., 1897, 69, 1397, 1402), and is converted by triethylamine in the presence of benzene into a mixture of *ketopinic anhydride*, m. p. 182°, and *dinorcamphocyclohexanedione* (annexed formula),

m. p. 98°. The latter substance is stable towards bromine or



permanganate, and does not react with hydrogen in the presence of palladium. It is not affected by boiling alkali hydroxide, but is slowly decomposed by boiling concentrated hydrochloric acid with re-formation of ketopinic acid. It reacts with phenylhydrazine and *p*-bromophenylhydrazine, without, however, yielding uniform products. It gives a *di-semicarbazone*, $\text{C}_{22}\text{H}_{30}\text{O}_4\text{N}_6$, m. p. 226°.

Hydropinenecarboxyl chloride, in which the ketonic group is not present, reacts very slowly with triethylamine under the customary conditions. The sole isolable product of the reaction is *hydropinenecarboxylic anhydride*, which appears to be a modification of the substance (m. p. 210°) described by Houben and Doescher (A., 1911, i, 61); it has m. p. 184—185° when crystallised from benzene, but this value rises to 207—209° when it is crystallised from alcohol.

H. W.

The Utilisation of Ethyl γ -Diethoxyacetoacetate for the Synthesis of Derivatives of Glyoxaline. An Attempt to Synthesise Histamine by a New Method. GEORGE W. PUCHER and TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1922, 44, 817—826).—An attempt has been made to alkylate ethyl acetoacetate or ethyl γ -diethoxyacetoacetate by means of bromomethylphthalimide, as a first step in a new method of synthesising histamine, but without success. This bromophthalimide reacts abnormally with the sodium salts of β -ketonic esters, with formation of phthalimide, whereas the higher homologue reacts normally giving phthalimido-derivatives.

It was found that an almost quantitative yield of hydroxy-methylphthalimide could be obtained by heating phthalimide under a reflux condenser with 10—15% formaldehyde solution. The hydroxy-compound is readily converted into bromomethylphthalimide by digesting it at 50—60° with 48% hydrobromic acid and concentrated sulphuric acid for two hours. The bromo-compound reacts with potassium thiocyanate in acetone, giving *phthalimidomethyl thiocyanate*, $\text{C}_6\text{H}_4(\text{CO})_2\text{N-CH}_2\text{SCN}$, m. p. 147—148°, which is extremely irritant to the eyes. In the same solvent with potassium iodide, it gives *iodomethylphthalimide*, m. p. 150° (cf. Gabriel, A., 1908, i, 181).

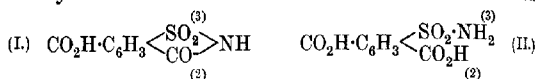
Bromoethylphthalimide reacts with the sodium salt of ethyl

γ -diethoxyacetoacetate, giving *ethyl α -phthalimidoethyl- γ -diethoxyacetoacetate*.
W. G.

Sulphamidophthalic Acid and Sulphimidophthalic Acid

TH. ZINCKE and H. GREUNE (*Annalen*, 1922, **427**, 221—255).

A considerable amount of confusion has arisen with regard to these two acids and their salts. For instance, all the salts of the imido-acid are described in "Beilstein's Handbuch" as salts of the amido-acid, which accords neither with the erroneous original literature nor with the truth. The two substances (formulae I and II) are dibasic acids of similar strength; both they and their salts are easily interconvertible, and the salts of the imido-acid frequently crystallise with H_2O , which makes it difficult to distinguish between them. The present paper places the whole chemistry of these substances for the first time on a correct basis.



The acid potassium salt which separates when the alkaline solution obtained by oxidising naphthalene-1-sulphonamide with alkaline permanganate is concentrated, cautiously acidified, and allowed to remain is the *N*-potassium salt of the imido-acid with $1H_2O$ which is quickly eliminated in a vacuum at 100° . The same substance is produced when the acid potassium salt (below) of the amido-acid is crystallised from warm water. When the *N*-potassium salt is treated with strong hydrochloric acid it gives the imido-acid (needles, decomp. 275 — 276° when quickly heated), but if boiled with *N*-hydrochloric acid it yields the amido-acid. The latter crystallises in leaflets or needles with $1H_2O$ which is given up slowly at 100° but quickly at 120° , the dried acid passing into the imido-acid with elimination of a further molecule of H_2O at 194° . It is a slightly stronger acid than the imido-acid, into which it is converted on warming with concentrated hydrochloric acid. The carboxyl-potassium salt of the imido-acid is obtained by heating the acid potassium salt of the amido-acid at 150° ; it is easily soluble in water, but on warming its solution the less soluble *N*-potassium salt of the imido-acid is precipitated. The normal barium salt of the imido-acid (needles, with $2H_2O$ which is given up in a vacuum at 100°) is prepared by adding the imido-acid to excess of barium hydroxide. The *N*-silver salt of the imido-acid (needles, with $1H_2O$ which is eliminated in a vacuum at 100°) is prepared from the *N*-potassium salt, and the carboxyl-silver salt (amorphous) of the imido-acid by heating the acid silver salt of the amido-acid at 150° , or by precipitation from a solution of the carboxyl-potassium salt of the imido-acid. The normal silver salt of the imido-acid is obtained by precipitation from a neutralised solution of the *N*-potassium salt.

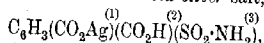
The *N*-methyl ester (needles, m. p. 189°) of the imido-acid is prepared from the *N*-potassium or *N*-silver salt and methyl iodide, but the reaction does not proceed very smoothly. It is rather

stable towards hydrolysing agents, but its constitution may be established by hydrolysis with concentrated hydrochloric acid at 150°, when methylamine is eliminated. The carboxyl-*methyl* ester (needles, m. p. 184—185°) of the imido-acid is prepared either from the carboxyl-*silver* salt and methyl iodide, or by heating the acid methyl ester (below) of the amido-acid, or by cautious alkaline hydrolysis of the dimethyl ester (below) of the amido-acid. Both this ester and the carboxyl-*ethyl* ester of the imido-acid give the imido-acid itself on hydrolysis by means of 2*N*-sodium hydroxide. The dimethyl ester (needles, m. p. 176°) of the imido-acid is prepared from the normal potassium or silver salt. An isomeric ester,

dimethyl ψ-sulphimidophthalate, $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_3\text{<}\begin{array}{c} \text{SO}_2 \\ \text{C(OMe);N} \end{array}$ (small

tablets, m. p. 163°), is obtained by the action of methyl alcohol on *ψ-sulphimidophthalyl dichloride* (needles, m. p. 156°), which is prepared from the imido-acid by heating with phosphorus pentachloride at 150—160°. The *diethyl ψ*-ester (small tablets, m. p. 142—143°) is obtained in a similar way, using ethyl alcohol, and the *diamide* (fine needles, m. p. above 280°) using ammonia. These derivatives of the *ψ*-imide are all easily hydrolysed to the imido-acid.

The acid *potassium* salt, $\text{C}_6\text{H}_3(\text{CO}_2\text{K})^{(1)}(\text{CO}_2\text{H})^{(2)}(\text{SO}_2\cdot\text{NH}_2)^{(3)}$, of the amido-acid is prepared by cautious half-neutralisation of the acid with potassium hydroxide. On warming with water, it passes into the *N*-potassium salt of the imido-acid. The normal barium salt is precipitated when barium chloride is added to an ammoniacal solution of the amido-acid. The acid *silver* salt,



and the normal *silver* salt are obtained from the corresponding alkali salts.

The acid *methyl* ester, $\text{C}_6\text{H}_3(\text{CO}_2\text{Me})^{(1)}(\text{CO}_2\text{H})^{(2)}(\text{SO}_2\cdot\text{NH}_2)^{(3)}$ (small, glistening needles, m. p. 205°), may be prepared either by heating the amido-acid with methyl alcohol, or from the acid silver salt by heating with methyl iodide. On hydrolysis by alkalis or dilute acids, it yields the amido-acid; cold concentrated hydrochloric acid converts it into the imido-acid. The dimethyl ester (m. p. 148°) of the amido-acid may be obtained by esterifying either the amido-acid or the imido-acid by means of methyl alcohol and hydrogen chloride, or by heating the normal silver salt of the amido-acid with methyl iodide. The diethyl ester has m. p. 104—105°.

C. K. I.

The Configuration of the β-Phenylglyceric Acids and Phenylglycidic Acid. J. BÖESEKEN [and C. DE GRAAFF] (*Rec. trav. chim.*, 1922, 41, 199—207).—Of the two isomeric forms of β-phenylglyceric acid, melting at 141° and 122°, respectively, the former shows a greater increase in conductivity under the influence of boric acid and the structure in which the hydroxyl groups are

most closely associated should therefore be assigned to it (cf. A., 1921, i, 843, 844). The dissociation constants of these acids are, for the former 2.35×10^{-4} and for the latter 2.54×10^{-4} ; it is probable that the phenyl and carboxyl groups are closer in the latter.

The oxidation of cinnamic acid by potassium permanganate to β -phenylglyceric acid takes place at a low temperature without molecular inversion. In β -phenylglycidic acid the phenyl and carboxyl groups are in the *trans*-position with respect to the triatomic ring. This acid in acid solution is hydrated, yielding the β -phenylglyceric acid of m. p. 141° ; in alkaline solution the isomeride (m. p. 122°) is formed and in this case molecular inversion occurs.

H. J. E.

The Action of Bromine on certain δ -Ketonic Esters. E. P. KOHLER (*J. Amer. Chem. Soc.*, 1922, 44, 840—847).—It has previously been shown that methyl γ -benzoyl- β -phenylethylmalonate on bromination in methyl alcohol gives one monobromo-derivative and in chloroform a mixture of two monobromo-derivatives (cf. A., 1911, i, 984; 1917, i, 566, 568). The constitution of these two derivatives has now been determined, and a third isomeride has been prepared. The bromide, m. p. 113° (*loc. cit.*), is an α -bromo-derivative and the other bromide, m. p. 102° (*loc. cit.*, m. p. was given as 98°), and the new isomeride are stereoisomeric γ -bromo-derivatives. The γ -bromo-compound, m. p. 102° , on further bromination, yields three dibromides, two of which have already been described (*loc. cit.*), whilst the third, methyl $\gamma\gamma$ -dibromo- γ -benzoyl- β -phenylethylmalonate, has m. p. 126° , and when boiled with alcoholic potassium iodide yields methyl γ -bromo- γ -benzoyl- β -phenylethylmalonate, m. p. 76 — 77° .

On heating at from 150° to 200° , the two monobromo-derivatives, m. p. 102° and 77° , respectively, readily decompose, giving, amongst other products, methyl γ -benzoyl- β -phenylbutyrolactone- α -carboxylate, m. p. 93° , but the derivative, m. p. 113° , is much more stable and undergoes complex changes only at much higher temperatures.

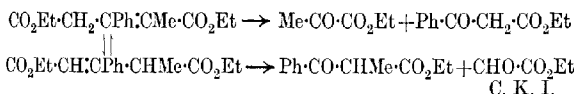
If in these δ -ketonic esters prepared from malonic esters and $\alpha\beta$ -unsaturated ketones the α -position is blocked by a methyl group, the ester only gives one monobromo-derivative on bromination. Thus methyl γ -benzoyl- β -phenylethylmethylmalonate, m. p. 121 — 122° , obtained from phenyl styryl ketone and methyl malonate, gives methyl γ -bromo- γ -benzoyl- β -phenylethylmethylmalonate, m. p. 156 — 157° ; methyl γ -4-bromobenzoyl- β -phenylethylmethylmalonate, m. p. 89° , gives methyl γ -bromo- γ -4-bromobenzoyl- β -phenylethylmethylmalonate, m. p. 140° ; methyl γ -4-methoxybenzoyl- β -phenylethylmethylmalonate, m. p. 120 — 122° , gives methyl γ -bromo- γ -4-methoxybenzoyl- β -phenylethylmethylmalonate, m. p. 151° . On heating, methyl γ -bromobenzoyl- β -phenylethylmethylmalonate yields methyl γ -benzoyl- β -phenyl- α -methylbutyrolactone- α -carboxylate, m. p. 108° .

W. G.

α -Carboxy- β -phenyl- α -methylglutaconic Esters and the Isomerism of the Phenylglutaconic Acids. FRANZ FEIST, PAUL KARL BRENER, and BERNH. LUBRICHT (*Annalen*, 1922, **428**, 40—59; cf. this vol., i, 521; Thorpe and Wood, T., 1913, **103**, 1574).—The action of ozone on the solid and liquid forms of ethyl α -carboxy- β -phenyl- α -methylglutaconate indicates that both these substances have the constitution assigned, since they yield additive products with this reagent. The solid (*trans*-) ester yields an oily *perozonide*, $C_{19}H_{24}O_{13}$, which when heated with water breaks down into carbon dioxide, hydrogen peroxide, ethyl α -methylbenzoyl-malonate (?), and ethyl glyoxylate, which is at once oxidised to oxalic acid. The liquid (*cis*-) ester gives a small amount of a normal *ozonide*, $C_{19}H_{24}O_9$, m. p. 144°, and an oily *perozonide*, which on hydrolysis yield carbon dioxide, hydrogen peroxide, ethyl methylmalonate, and benzoic, succinic, oxalic, and acetic acids.

Thorpe and Wood prepared three β -phenyl- α -methylglutaconic acids (termed normal, *cis*-, and *trans*-) by hydrolysis of these esters. The present authors cannot obtain the "normal" or the "*cis*-" acids but they isolate a new isomeride, m. p. 151°. This they term *cis*- β -phenyl- α -methylglutaconic acid, the suggestion being that Thorpe and Wood's *cis*- and normal acids were mixtures.

cis- and *trans*- β -Phenyl- α -methylglutaconic acids both yield oily ozonides, which on hydrolysis give carbon dioxide, hydrogen peroxide, ketones, and benzoic, oxalic, and acetic acids. *Ethyl trans- β -phenyl- α -methylglutaconate*, b. p. 191–192°/14, yields an oily perozonide and a solid ozonide, $C_{18}H_{20}O_7$, m. p. 142°, which on hydrolysis yield ethyl pyruvate, ethyl α -benzoylpropionate, ethyl benzoylacetate, and ethyl glyoxylate (which becomes oxidized to oxalic acid). *Ethyl cis- β -phenyl- α -methylglutaconate*, b. p. 184–185°/16 mm., 214°/40 mm., 220°/53 mm., gives the same ultimate products. These facts are explicable on the theory that the esters are tautomeric:



Preparation of Derivatives of Cholic Acid. J. D. RIEDEL, ART.-GES. (D.R.-P. 339350; from *Chem. Zentr.*, 1921, iv, 1227; cf. A., 1921, i, 540).—Cholic acid is treated with dehydrating agents, for example, inorganic acids, potassium hydrogen sulphate, organic acids such as glycollic acid, and oxalic acid. A mixture is obtained of apocholic acid and other unsaturated acids. For example, cholic acid is dissolved in glycollic acid, fused potassium pyrosulphate is added, and the mixture heated at about 130°. After removal of the dehydrating agents, the acids are dissolved in sodium hydroxide solution. With acetic acid an additive compound is obtained in needles, m. p. 150–160°, after sintering. The free apocholic acid has m. p. 173–176° after sintering. By dehydrating cholic acid with 15% sulphuric acid a syrupy mass is obtained, from which, after washing with water, dissolving in sodium carbonate solution,

and precipitating with dilute hydrochloric acid, a mixture of the unsaturated acids is obtained. *apoCholic* acid is separated by its relative insolubility in ether. The stronger unsaturated acids are obtained by dissolving the yellow, resinous residue after the evaporation of ether in sodium carbonate solution and precipitating with dilute hydrochloric acid. The unsaturated acids may also be prepared by heating cholic acid and oxalic acid at 100°.

G. W. R.

Preparation of Derivatives of Cholic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co., D.R.-P. 339561; from *Chem. Zentr.*, 1921, iv, 1227).—Paraformaldehyde intimately mixed with cholic acid is heated at 160–170° for half an hour. The cooled mass, after extraction with dilute sodium carbonate solution, is dissolved in ethyl alcohol, and the filtered solution mixed with ice-cold water. A *methylene* compound is thus obtained as a white, tasteless powder, m. p. 170°. It has therapeutic uses.

G. W. R.

Bile Acids. XI. The Oxidation of Cholic Acid. HEINRICH WIELAND and OTTO SCHLICHTUNG (*Z. physiol. Chem.*, 1922, 119, 76–97).—Biloidanic acid, prepared by the oxidation of bilianic acid, has been given the formula $C_{19}H_{28}O_{10}$ by Letsch (A., 1909, i, 697) and by Schenck (A., 1921, i, 197). Borsche, Weickert, and Meyer (this vol., i, 255) found for it the formula $C_{18}H_{26}O_{10}$. The authors have prepared biloidanic acid, the neutral hexamethyl ester, the triethyl and monoethyl esters, trimethyl, dimethyl, and monomethyl esters, and the analytical results agree completely with the formula $C_{23}H_{34}O_{12}$ for the parent acid. Letsch has also described a hydrated form of biloidanic acid to which he assigned the formula $C_{19}H_{28}O_{10} \cdot 2H_2O$, but it is now found to be $C_{23}H_{34}O_{12} \cdot 2H_2O$. When heated in a vacuum at 115–125° this loses, however, $3H_2O$, pointing to anhydride formation from two of the carboxyl groups.

The constitution of the bile acids is considered in relation to these results.

W. O. K.

Preparation of Bile Acids. J. D. RIEDEL, AKT.-GES. (D.R.-P. 338736; from *Chem. Zentr.*, 1922, iv, 1226–1227).—The unsaturated acid (*apocholic* acid) obtained by the elimination of water from cholic acid or its esters, is combined with hydrocarbons or their derivatives such as alcohols, bases, aldehydes, ketones, acids, and esters. For example, the unsaturated acid obtained by the elimination of water from methyl cholate is warmed with 96% acetic acid. On cooling, an *additive* compound crystallises, having an ill-defined m. p. 135–155°. The acetic acid is completely removed by excess of alkali or ammonia. The *additive* compound with 2 molecules of *apocholic* acid and 1 molecule of naphthalene gives crystals having m. p. 173–174°; it is odourless and stable in air. A clear solution is given in water on addition of sodium carbonate and a small quantity of sodium *apocholate*. The equimolecular *additive* compound of camphor and *apocholic* acid is soluble in dilute alkalis and bases. Other additive compounds mentioned are *strychnine-apocholic* acid, *ethyl acetate-apocholic* acid, and

benzaldehyde-apocholic acid; the latter forms colourless needles, m. p. 156°. *apoCholic acid ethyl alcoholate* crystallises in needles which decompose in air with loss of alcohol. The compounds may also be prepared by way of the acetic acid compound. They have therapeutic uses.

G. W. R.

Vanillin Isomerides of the Resorcylic Series. ERWIN OTT and ERNST NAUEN (*Ber.*, 1922, 55, [B], 920—929).—Considerable uncertainty exists with regard to the constitution of the mono-methyl ethers of β -resorcylic aldehyde [2 : 4-dihydroxybenzaldehyde], three substances, m. p. 41—42°, 62—63°, and 153°, respectively, having been thus described. The last-mentioned has been stated by Gattermann (*A.*, 1908, i, 28) to be the sole product of the action of hydrogen cyanide, hydrogen chloride, and aluminium chloride on resorcinyl monomethyl ether (this does not appear to be actually the case, since it is now found that the substance, m. p. 41—42°, is formed to a less extent); this substance is characterised as 4-hydroxy-2-methoxybenzaldehyde by its further methylation with methyl sulphate and cold alkali hydroxide to 2 : 4-dimethoxybenzaldehyde, m. p. 68°. The product, m. p. 41—42°, is also converted by the action of methyl sulphate on its sodium salt suspended in toluene at 40° into 2 : 4-dimethoxybenzaldehyde, and hence is shown to be 2-hydroxy-4-methoxybenzaldehyde. The aldehyde, m. p. 62—63°, is too sensitive towards alkali to permit its further methylation with methyl sulphate and, as in the case of the compound, m. p. 41—42°, diazomethane is found to be an unsuitable reagent for the methylation of difficultly substituted phenolic groups even at 100°. Friedländer's view (*A.*, 1908, i, 674) that the products, m. p. 41—42 and 62—63°, are actually identical is disproved by the observation that the corresponding oximes melt at 124—126° and 138°, respectively. The explanation of the difficulty is found in the fact that analysis of the aldehyde, m. p. 62—63°, obtained by the action of methyl iodide shows that it contains two methyl groups, of which only one is removable by hydriodic acid; the second methyl group must therefore be attached to the nucleus. The small amount of available material has precluded the exact elucidation of the constitution of the compound, but, by analogy, it is considered to be 2-hydroxy-4-methoxy-3-methylbenzaldehyde; the presence of substituents in the two ortho-positions to the hydroxyl group explains satisfactorily the impossibility of its further methylation and the non-appearance of acidic characteristics.

The following modification of Wegscheider's process is recommended for the oximation of hydroxyaldehydes, which are very sensitive towards alkali hydroxide. Hydroxylamine hydrochloride is dissolved in the minimum quantity of water, and the solution is treated with ammonia solution (20%) until it is just neutral towards litmus paper. An alcoholic solution of the aldehyde is added and the mixture is preserved at the atmospheric temperature until reaction is complete, after which the oxime is precipitated by addition of water.

The preparation of resorciny methyl ether is effected conveniently by the treatment of resorcinol with sodium hydroxide solution (10%) and methyl sulphate. The solution is made strongly alkaline and the dimethyl ether is removed by distillation with steam; subsequently the residue is acidified and again treated with steam, thus giving the monomethyl ether and leaving the non-volatile unattacked resorcinol.

H. W.

Preparation of Protocatechualdehyde. S. HAMBURGER (D.R.-P. 339945; from *Chem. Zentr.*, 1921, iv, 1223—1224; cf. Schmidt, A., 1913, i, 682).—A modification of an earlier patent, whereby thionyl chloride is substituted for phosphorus pentachloride. Thionyl chloride and chlorine are allowed to act either successively or simultaneously on piperonal, with or without the use of solvents. For example, piperonal is treated with thionyl chloride and then warmed at 100°. Chlorine is passed in, the *dichloropiperonyl chloride* formed is decomposed with water, and the protocatechualdehyde formed is extracted with ether or obtained by evaporation.

G. W. R.

Transformation of Tertiary Ethinylcarbinols into Unsaturated Ketones. KURT H. MEYER and KURT SCHUSTER (*Ber.*, 1922, 55, [B], 819—823).—Diphenylphenylethinylcarbinol, $\text{CPh:C(CPh)}_2\text{OH}$, is converted by acetyl chloride, acetic anhydride, thionyl chloride, hydrogen chloride dissolved in anhydrous ether, or concentrated sulphuric acid into phenyl β -phenylstyryl ketone, yellow prisms, m. p. 86—87° [Kohler (A., 1905, i, 215) gives m. p. 92°]; the constitution of the ketone is established by its oxidation to benzophenone and benzoic acid and hydrogenation to $\beta\beta$ -diphenylpropiofenone, m. p. 94—95°. The transformation might be due to the migration of a phenyl or a hydroxyl group; the latter is shown to be the case, since *di-p-chlorophenylphenylethinylcarbinol*, $\text{CPh:C(C}_6\text{H}_4\text{Cl)}_2\text{OH}$, short, colourless prisms, m. p. 163—164°, is converted under similar conditions into *phenyl di-p-chloro- β -phenylstyryl ketone*, $\text{C(C}_6\text{H}_4\text{Cl)}_2\text{CH-COPh}$, yellow crystals, m. p. 103—104°, the constitution of which is established by its oxidation to 4:4'-dichlorobenzophenone and benzoic acid. The mechanism of the change has not been elucidated.

H. W.

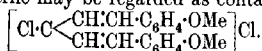
Halochromism and "Solvatochromism" of Distyryl Ketone and Simpler Ketones and of their Ketonic Chlorides. A. HANTZSCH (*Ber.*, 1922, 55, [B], 953—979).—In the so-called halochromism of ketones and ketonic chlorides two optically and chemically different processes are to be distinguished, (1) solvatochromism caused by the formation of additive products which involves a relatively small alteration in the absorption of light, and (2) the actual halochromism due to the formation of additive products with marked alteration in the absorption of light corresponding with the greater chemical change involved by the formation of complex carbonium salts under the transforming influence of acids. Generally, the two processes are closely related frequently in the sense that solvatochromism is the precursor of halochromism.

Thus, the solvatochromic additive products of certain ketones with stannic chloride are converted by hydrogen chloride into the halochromic carbonium salts, and hence the ketonic chlorides obtained from the ketones are directly converted by stannic chloride into the halochromic salts. The well-defined additive compounds which are constant in composition represent the extreme case of solvatochromism in the one direction (solid solvates), whereas the other extreme is represented by unsaturated substances which dissolve in such solvents as ether with deepening of colour and the formation of unstable compounds which either cannot be isolated in the solid state or in which the components appear to be present in indefinite ratio.

The absorption spectrum of distyryl ketone in ether differs considerably from that of triphenylcarbinol in ethyl alcohol, and it is therefore the more remarkable that the substances exhibit very similar absorption when dissolved in sulphuric acid. It appears therefore to be probable that the salts are similarly constituted and they may be formulated $\left[\text{Ph} \cdot \text{C} < \begin{smallmatrix} \text{Ph} \\ \text{Ph} \end{smallmatrix} \right] \text{X}$ and $\left[\text{R} \cdot \text{C} < \begin{smallmatrix} \text{CH} \cdot \text{CHPh} \\ \text{CH} \cdot \text{CHPh} \end{smallmatrix} \right] \text{X}$ or $\left[\text{CHPh} \cdot \text{CH} \cdot \text{CR} \cdot \begin{smallmatrix} \text{CH} \\ \text{Ph} \end{smallmatrix} > \text{CH} \right] \text{X}$ (in which R = H, OH, Cl or SO_4H).

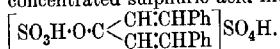
The choice between the two latter alternatives cannot be made definitely, but reasons are advanced for preferring the more symmetrical. The salts from benzophenone and benzophenone chloride are genetically intermediate between the triphenylcarbonium salts and those derived from distyryl ketone. Purely chemical evidence of the complex constitution of these halochromic salts can be adduced in the same manner as for the triphenylcarbonium compounds. The most important observation in this connexion is that the characteristic properties of the phenyl residue and of the $-\text{C} \cdot \text{C}-$ group appear in them to be masked and, to some extent, completely lost. Thus the phenyl groups of triphenylcarbonium or distyryl ketone appear nearly indifferent towards concentrated sulphuric acid. Unsaturated ketones which instantly unite with bromine in glacial acetic acid are only very slowly attacked by bromine when dissolved in concentrated sulphuric acid; this is true even for the four ethylenic bonds of the dark violet salts of dicinnamylidenemethyl ketone, $\left[\text{HO} \cdot \text{C} < \begin{smallmatrix} \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CHPh} \\ \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CHPh} \end{smallmatrix} \right] \text{SO}_4\text{H}$.

The halochromism of the "abnormal" ketonic chlorides derived from styryl methyl ketone and similar substances which have been shown by Straus and Dützmann (this vol., i, 148) to have the constitution, $\text{CHAr} \cdot \text{CH} \cdot \text{CCl} \cdot \text{CH} \cdot \text{CHCl} \cdot \text{Ar}$, is exactly analogous to that of the triphenylmethyl haloids, and the coloured solution formed, for example, by the chloride of dianisylidenemethyl ketone in phenylacetonitrile may be regarded as containing the salt



Since, however, the absorption spectra of the ketones in acid solution is exactly similar to those of the salts of the corresponding ketonic chlorides, the salts of the former may be regarded as having

initially the constitution $\left[\text{HO}-\text{C} < \begin{smallmatrix} \text{CH}:\text{CHPh} \\ \text{CH}:\text{CHPh} \end{smallmatrix} \right] \text{SO}_4\text{H}$ and passing by further action of concentrated sulphuric acid into



Benzophenone when dissolved in concentrated sulphuric acid behaves like the almost completely ionised sulphate of sodium, dimethylpyrone or ethyl ether, and its salt is therefore formulated $[\text{Ph} \cdot \text{C}(\text{OH})\text{Ph}]\text{SO}_4\text{H}$, the hydroxyl group being in this case not appreciably esterified. The initially much more intensely yellow solution of benzophenone chloride in concentrated sulphuric acid contains the salt $(\text{Ph} \cdot \text{CCl} \cdot \text{Ph})\text{HSO}_4$, but rapidly becomes decolorised with liberation of hydrogen chloride and formation of the hydroxy-salt.

With regard to the solvatochromism of distyryl ketone and related ketones, it is pointed out that the optical changes are different from and generally more simple than those connected with halochromism. In these cases, compounds are being dealt with which are generally highly dissociated even in indifferent solvents such as chloroform. The characteristic absorption spectra are therefore obtained only when one component is added in such excess that optical constancy is induced. Thus, cinnamaldehyde, which forms a solid additive product, $(\text{CHPh}:\text{CH}:\text{CHO})_2\text{SnCl}_4$, with stannic chloride, is but little affected optically when dissolved with twenty molecular proportions of stannic chloride in chloroform, and the spectrum gradually changes with further addition of stannic chloride, ultimately becoming constant when 8.50 molecular proportions of the latter have been added. Similar observations are recorded with salicylaldehyde, benzophenone, or distyryl ketone with stannic chloride in chloroform solution. H. W.

The Active Constituents of the True Coto-bark. The Synthesis of Cotoin. ERNST SPÄTH and KARL FUCHS (*Monatsh.*, 1921, **42**, 267—272).—Attempts to synthesise cotoin, which is a monomethyl ether of 2 : 4 : 6-trihydroxybenzophenone, by methylation of the trihydroxy-compound with methyl alcohol and hydrochloric acid were unsuccessful, the only product isolated being methyl benzoate. The synthesis was accomplished by methylating with diazomethane in ethereal solution at -12° . Although less than one molecular proportion of diazomethane was used, the product contained 36% of cotoin, 26% of hydrocotoin (6-hydroxy-2 : 4-dimethoxybenzophenone), and 2% of the trimethoxy-compound. The synthesis does not establish the orientation of the methoxyl group in cotoin, although it is probable that methylation occurs first in the para-position. E. H. R.

The Hydroxybenzoylphloroglucinols. HIDEJIRO NISHIKAWA and ROBERT ROBINSON (*I.*, 1922, **121**, 839—843).

Singular Formation of Ketodinitrones and their Behaviour. L. ALESSANDRI (*Gazzetta*, 1922, **52**, i, 193—199).—At the ordinary temperature and best in a solvent which is indifferent to or at

least difficultly oxidised by nitrosobenzene, the latter (2 mols.) and toluene (1 mol.) react very slowly with formation of the *dinitrone*, $\text{O:NPh:CPh:CPh:NPh:O}$, which separates in pale yellow crystals decomposing with liberation of gas at 222° . When boiled with dilute sulphuric acid, the dinitrone yields benzil and *p*-aminophenol, the latter resulting from transposition of the β -phenylhydroxylamine originally formed. Reduction of the dinitrone by means of aluminium amalgam gives the dianil of benzil. The action of hydroxylamine on this ketodinitrone differs from that observed by Angeli, Alessandri, and Pegna with the aldonitrones (A., 1910, i, 552, 752) and is one of reduction, the product being either the semi-reduced compound, NPh:CPh:CPh:NPh:O , or an additive compound of the dinitrone with the dianil of benzil.

In the above formation of the ketodinitrone, the nitrosobenzene acts as an unsaturated compound, that is, as the phenyl ether of the anhydride of dihydroxyammonia, NPh:O .

The action of magnesium phenyl bromide on the aldodinitrone described by von Pechmann (A., 1898, i, 75, 187) might be expected to yield the corresponding $\beta\beta$ -dihydroxylamine, and this by oxidation the ketodinitrone, thus: $\text{O:NPh:CH:CH:NPh:O} + 2\text{MgPhBr} \rightarrow [\text{OH:NPh:ChPh}]_2 \rightarrow \text{O:NPh:CPh:CPh:NPh:O}$. The first of these reactions gives a small yield of a colourless compound, m. p. about 156° , which may be the $\beta\beta$ -dihydroxylamine, but the oxidation of the latter appears to give phenyl-*N*-phenylnitron or the *N*-phenyl ether of benzaldoxime, CHPh:NPh:O , this being obtained in appreciable yield. The latter compound is obtainable also by oxidation of the simpler β -hydroxylamine, $\text{CH}_2\text{Ph:NPh:OH}$ (cf. Cusmano, "Catalytic Reduction of Nitrones," to be published later).

Nitrosobenzene reacts on phenylpropionic acid with extreme slowness, if at all. With acetylene compounds containing unreplaced hydrogen, the action of nitrosobenzene appears to follow a different course. With acetylene itself in acetone solution, the reaction is very slow, but may be catalysed by alcoholic potassium hydroxide, and then yields a very small proportion of oxanilide, which is isomeric with the aldodinitrone, O:NPh:CH:CH:NPh:O , expected.

T. H. P.

Derivatives of 2-Hydroxybenzanthrone. I. GEOFFREY GORDON BRADSHAW and ARTHUR GEORGE PERKIN (T., 1922, 121, 911—922).

Preparation of Anthraquinone and its Derivatives. CHEMISCHE FABRIK WORMS AKT.-GES. (Brit. Pats. 156215 and 156338).—Anthraquinone or its derivatives are obtained by passing oxygen under pressure into a solution or suspension of anthracene (or its derivatives) in the presence of a small proportion of fuming nitric acid or an oxide of nitrogen at 80 — 90° . An additional oxygen carrier, for example, cobalt nitrate, may also be added if desired. The oxygen is rapidly absorbed and the operation is complete in three to five hours. When nitric acid is employed and the water formed in the reaction is not removed, nitro-compounds and other

impurities from which the anthraquinone can only be freed with difficulty are formed. This can be avoided and anthraquinone of 99—100% purity obtained if the nitric acid is replaced by sodium nitrite and the reaction is carried out in presence of a dehydrating agent such as acetic anhydride or anhydrous sodium acetate [cf. *J. Soc. Chem. Ind.*, 1922, 407A].

G. F. M.

Manufacture of Hydroxy- and Sulphohydroxy-derivatives of Anthraquinone. DAVID SEGALLER, DAVID HENRY PEACOCK, and BRITISH DYESTUFFS CORP., LTD. (Brit. Pat. 176925).—1-Hydroxyanthraquinone-4-sulphonic acid is obtained by the condensation of phenol or phenol-*p*-sulphonic acid with phthalic anhydride by means of a sulphuric acid solution of boric acid at about 200°. On further treatment of this substance, either after isolation, or in the sulphuric acid solution in which it is obtained, at a temperature of about 240—250°, it is converted into 1:4-dihydroxyanthraquinone (quinizarin). If phenol-2:4-disulphonic acid is used as starting material, the final product consists essentially of 1:2:4-trihydroxyanthraquinone (purpurin), whilst if *o*- or *m*-cresols are employed, β -methylquinizarin is produced. From *p*-cresol, 1-hydroxy-4-methylanthraquinone is obtained.

G. F. M.

Preparation of Borneol. FABRIQUES DE PRODUITS CHIMIQUES DE THANN ET DE MULHOUSE (Brit. Pat. 164302, addn. to 144604; cf. A., 1921, i, 425).—In the preparation of bornyl tetrachlorophthalate from turpentine in presence of an organic solvent, the secondary products obtained from previous operations consisting of unchanged pinene mixed with dipentene may advantageously be used as diluent instead of ether, etc. A similar yield of borneol is obtained, and as the dipentene takes no part in the reaction the amount present in the recovered hydrocarbon increases from operation to operation until the quantity is such that it may easily be separated by fractional distillation from the crude secondary product.

G. F. M.

Higher Terpene Compounds. III. The Naphthalene Hydrocarbons Cadalene and Eudalene. Two Aromatic Fundamental Compounds of the Sesquiterpene Series. L. RUZICKA, JULES MEYER, and M. MINGAZZINI (*Helv. Chim. Acta*, 1922, 5, 345—368; cf. this vol., i, 547).—The previous position of sesquiterpene chemistry is shortly reviewed. The method of removing hydrogen from cadinene by heating it with sulphur (A., 1921, i, 573) has been applied to other cases. The relative arrangement of the carbon atoms in a compound is unchanged by this treatment, since limonene and terpinene are each converted by its means into *p*-cymene, the respective yields being 15% and 50%. This result suggests that compounds containing cyclic double bonds may in general be more easily dehydrogenated than those with unsaturated side chains. Further, all the sesquiterpene fractions of a given oil yield the same product, and in no case is evidence observed of the formation of mixtures. Hence even

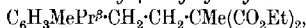
f, in any such case, the oil itself should be a mixture, the same carbon skeleton is present in each component. The hydrocarbon from cadinene (*loc. cit.*) is now termed *cadalene*; it has also been obtained from tetrahydrocadinene, from calamenol and its degradation product calamene, from calamenene, from *isozingiberene*, and from the sesquiterpene alcohol from Javanese citronella oil. Its smooth formation from the monocyclic zingiberene shows that the formation of a naphthalene derivative by this reaction is to be understood as evidence that the compound under examination has a potential, rather than an actual, bicyclic structure. Endesmol and selinene apparently react according to the respective equations: $C_{15}H_{24}O + 3S = C_{14}H_{16} + H_2O + 2H_2S + CH_3SH$; $C_{15}H_{24} + 3S = C_{14}H_{16} + 2H_2S + CH_3SH$; the same hydrocarbon, eudalene, being produced in each case. This exceptional behaviour suggests that these compounds each contain a methyl group which cannot survive the transition into an aromatic compound and that the cadinene group of sesquiterpenes (Semmler and Becker, A., 1913, i, 742; Semmler and Stenzel, A., 1915, i, 427) must be sub-divided into the eudalene and cadalene classes. *Eudalene*, b. p. 280—281°, d_4^{20} 0.9734, R_D 63.31, ER_D 3.21, E_{25}^D 1.74 (*picrate*, $C_{20}H_{18}O_7N_3$, orange-yellow needles, m. p. 90—91°; *styphnate*, $C_{26}H_{18}O_8N_3$, yellow needles, m. p. 119—120°), is stable towards bromine and cold potassium permanganate, and its physical constants agree well with those of a naphthalene hydrocarbon. The synthesis of cadalene (see following abstract) shows it to be 1:6-dimethyl-4-isopropyl-naphthalene. Further, the close relationship of cadinene to copaene, and the loss of three carbon atoms from the molecule of copaenecetic acid by oxidation with sodium hypobromite (Semmler and Stenzel, *loc. cit.*) indicate that one double bond in cadinene is situated at the carbon atom carrying the *isopropyl* group. Corresponding with the contrast between retene and its parent phenanthrene in respect of the lability of the primary oxidation products of the former, those of cadalene are less stable than those of naphthalene. The quinone formed by the oxidation of cadalene could only be detected by means of its *oxime*, $C_{15}H_{17}O_2N$, m. p. 178—179° (decomp.); 6-methyl-4-isopropyl-1-naphthoic acid, $C_{15}H_{16}O_2$, leaflets, m. p. 161—162°, and possibly a hydroxyquinone, with other products were also formed. The relationship of the open-chain compound farnesol (Kerschbaum, A., 1913, i, 739) to cadalene is that of the aliphatic terpenes, for example, ocimene, to *p*-cymene. Further, the close relationship of cadalene not only to bicyclic, but also to monocyclic (zingiberene) and to tricyclic (copaene) sesquiterpenes reveals for the first time the analogous structure of a considerable number of sesquiterpenes, not only among themselves, but also with those of the terpenes. The common factor in the two series is the union of isoprene molecules, usually to a *p*-cymene skeleton. Probably a number of monocyclic sesquiterpenes represent a transition from farnesol to cadinene. The cadinene type is intermediate between the simple terpenes and the diterpenes (from which abietic acid is derived) and caoutchouc, which constitutes the highest member of the terpene series, and is

related to the others in being built up from isoprene molecules. Santonin, as a derivative of 1:4-dimethyl-6-isopropynaphthalene (Cannizzaro and Gucci, A., 1893, i, 665) is to be included with cadinene in the hydronaphthalene sub-group of bicyclic sesquiterpenes.

J. K.

Higher Terpene Compounds. IV. Synthesis of Cadalene.

L. RUZICKA and C. F. SEIDEL (*Helv. Chim. Acta*, 1922, 5, 369—375; cf. preceding abstract).—On the assumption that cyclic sesquiterpenes might have the same carbon chain as the open-chain alcohol, farnesol, it appeared that cadalene would be 1:6-dimethyl-4-isopropynaphthalene. The accuracy of this deduction has now been verified by the identity of the synthetic hydrocarbon with cadalene. Ethyl 2-cymylacetate, prepared from carvone by means of ethyl bromoacetate and zinc (Wallach, A., 1901, i, 156), was reduced by Bouveault's method to β -2-cymylethyl alcohol, $C_8H_3MePr^2 \cdot CH_2 \cdot CH_2 \cdot OH$, b. p. 145—150°/12 mm. Condensation of its bromide, $C_{12}H_{17}Br$, b. p. 145—148°/12 mm., with ethyl methylmalonate furnished methyl β -2-cymylethylmalonate,



b. p. 200—210°/12 mm., from which β -2-cymyl- α -methylbutyric acid, $C_8H_3MePr^2 \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CO_2H$, b. p. 200—201°/11 mm., was prepared. From its chloride, b. p. 165°/11 mm., and aluminium chloride, 5-keto-1:6-dimethyl-4-isopropyltetrahydronaphthalene, b. p. 160—170°/12 mm., was obtained. Reduction of this compound in alcoholic solution with sodium furnished as chief product, with a certain proportion of the pinacone, the corresponding secondary alcohol. Finally, a mixture of this compound with the hydrocarbon, resulting from its partial dehydration on distillation, was dehydrogenated at 180—210° by means of sulphur. The identity of the synthetic product with cadalene followed from a comparison of physical constants, picrates, and styphnates.

J. K.

The Action of Concentrated Sulphuric Acid on Natural and Artificial Caoutchoucs. II. F. KIRCHOF (*Kolloid Z.*, 1922, 30, 176—187; cf. A., 1921, i, 116).—Plantation pale crepe rubber is believed to have the composition $C_{20}H_{34}$. Under the action of cold concentrated sulphuric acid on its carbon tetrachloride solution for two hours, it undergoes conversion into an amorphous product of the composition $C_{10}H_{15}$, d 1.093—1.096, insoluble in chloroform. Gutta percha under similar conditions is converted into a product of unaltered composition, $C_{10}H_{16}$, soluble in chloroform. The behaviour of the former product towards bromine and sulphur with formation of compounds of the composition $C_{20}H_{30}Br_2$ and $C_{20}H_{30}S$ indicates the disappearance of three double bonds during the action of the acid. African rubber of the composition $C_{10}H_{16}$ gives rise to a similar series of products to plantation rubber. The latter type of rubber is believed to consist of spirally arranged closed chains, $C_{20}H_{32}$ or $C_{30}H_{48}$, which are held together in aggregates by partial valencies. To plantation rubber, a similar structure is attributed, consisting of aggregated, open-chain spirals

of the composition $C_{20}H_{34}$. The disappearance of the characteristic properties of rubber when the raw material is exposed to the action of sulphuric acid, or when vulcanised rubber hardens spontaneously, is ascribed to the development of tetramethylene rings, with loss of double bonds, by bridging.

On prolonged treatment in the undissolved state with cold sulphuric acid, plantation rubber is oxidised to a product, $C_{10}H_{14}O$, which is probably identical with the main product in the spontaneous oxidation of vulcanised rubber. Oxidation of the rubber by prolonged contact in benzene solution into sulphuric acid gives rise to an aldehydic acid, $C_{20}H_{30}O_3$, m. p. $95-96^\circ$ (crystalline *phenylhydrazone*, m. p. $120-124^\circ$). D. F. T.

The Essential Oil from *Blumen Malcomii*. JOHN LIONEL SIMONSEN and MADYAR GOPAL RAU (T., 1922, 121, 876-883).

Constituents of Saffron. I. Picrocrocin. E. WINTERSTEIN and J. TELECKY (*Helv. Chim. Acta*, 1922, 5, 376-381; *Z. physiol. Chem.*, 1922, 120, 141-166).—Picrocrocin (Kayser, A., 1885, 59) forms colourless crystals, m. p. $154-155^\circ$, $[\alpha]_D^{20}$, -50.3° , and on hydrolysis with 1% sulphuric acid solution furnishes 54% of sugar (calculated as dextrose), with a ketone, $C_{10}H_{14}O$, b. p. $93^\circ/14$ mm., n_D^{20} 1.5240, n_F-n_C 0.02283, d 0.985 (semicarbazone, $C_{11}H_{17}ON_3$, m. p. $162-163^\circ$). Its physical constants suggest that the latter belongs to the terpene series, and, like carvone, it furnishes an additive compound with hydrogen sulphide, m. p. 80° (decomp.). The sugar produced by hydrolysis furnishes an osazone, m. p. 205° , a phenylmethylhydrazone, m. p. 128° , and a corresponding osazone, m. p. 150° . Mannose, galactose, pentoses, and methyl-pentoses could not be detected, but tests for levulose gave a positive result. The specific rotation was that of a mixture of 81.7% dextrose with 18.3% *d*-fructose, but the analytical results from picrocrocin could not be reconciled with this conclusion. Crocin, the colouring matter of saffron, contrary to earlier statements, furnishes on hydrolysis not an essential oil, but dextrose and a deep red, insoluble compound, crocetin (Decker, A., 1914, i, 979). Oxalic acid and a colourless unknown compound have been obtained from the oxidation of this compound. J. K.

Salicin Thiocyanate and Disalicyl Sulphide. GÉZA ZEMPLEN and ALEX. HOFFMANN (*Ber.*, 1922, 55, [B], 992-997).—Tetra-acetylsalicyl bromide is converted by ammonium thiocyanate in the presence of anhydrous acetone into *tetra-acetylsalicyl thiocyanate*, $C_8H_7O_5Ac_4 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot SCN$, well-developed prisms, m. p. 135° , $[\alpha]_D^{20} +48.35^\circ$ when dissolved in chloroform. Somewhat unexpectedly, it is converted by methyl alcoholic ammonia into *disalicyl disulphide*, $S_2(CH_2 \cdot C_6H_4 \cdot O \cdot C_6H_4 \cdot O)_2$, m. p. 193° after slight previous softening, $[\alpha]_D^{20} -46.8^\circ$ when dissolved in glacial acetic acid; the substance can occasionally be isolated directly in the crystalline state, but, in general, is so prepared by the action of methyl alcoholic ammonia on the readily crystalline *octa-acetate*, long, slender needles, m. p. 188° , $[\alpha]_D^{20} +45.6^\circ$ in chloroform solu-

tion. The latter is hydrolysed by hydrochloric acid in the presence of alcohol to *di-o-hydroxybenzyl disulphide*, $S_2[CH_2 \cdot C_6H_4 \cdot OH]_2$, small prisms, m. p. 103° .
H. W.

New Derivatives of Salicin containing Nitrogen and Polynuclear Hydroxybenzylamines. GÉZA ZEMPLÉN and ALPHONS KUNZ (*Ber.*, 1922, 55, [B], 979–992).—An investigation of the products obtained by the action of ammonia or amines on tetra-acetylsalicin bromide (cf. Zemplén, A., 1920, i, 559).

Tetra-acetylsalicin bromide, $C_6H_7O_5Ac_4 \cdot O \cdot C_6H_4 \cdot CH_2Br$, reacts readily with ammonia in ethyl or methyl alcoholic solution, exchanging its bromine atom initially for the amino-group and suffering de-acetylation; as with alkyl haloid and ammonia, however, the reaction proceeds further with the formation of secondary and tertiary amines. In the present instance, the isolation of a pure primary amine was not found possible, but the solution of the reaction product slowly deposits *disalicinamine*, $NH(CH_2 \cdot C_6H_4 \cdot O \cdot C_6H_{11}O_5)_2$, colourless needles, m. p. 205° (decomp.) after becoming yellow at 200° , $[\alpha]_D^{25} - 45.82^\circ$ in aqueous *N*-hydrochloric acid solution, which is hydrolysed by boiling hydrochloric acid to dextrose and *di-o-hydroxybenzylamine*, colourless needles, m. p. 168° . The mother-liquors from the secondary amine contain *trisalicinamine*, which is isolated as the *dodeca-acetyl* derivative, $N(CH_2 \cdot C_6H_4 \cdot O \cdot C_6H_7O_5Ac_4)_3$, microscopic needles, m. p. $173-175^\circ$, $[\alpha]_D^{25} - 45.13^\circ$ when dissolved in chloroform. It is hydrolysed by dilute hydrochloric acid to dextrose, acetic acid, and *tri-o-hydroxybenzylamine hydrochloride*, small, coarse needles, incipient decomp. 110° .

The reaction between tetra-acetylsalicin bromide and methylamine proceeds in an analogous manner, yielding (with de-acetylation) a non-crystalline syrup which, after re-acetylation, is readily separated into two fractions. The first of these consists of *penta-acetylsalicinmethylamine*, $C_6H_7O_5Ac_4 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot NMeAc$, coarse platelets, m. p. 165° , $[\alpha]_D^{25} - 38.49^\circ$ in chloroform solution, which is hydrolysed by acids to *o-hydroxybenzylmethylamine* (isolated as the *phosphotungstate* and analysed as the *hydrochloride*, $OH \cdot C_6H_4 \cdot CH_2 \cdot NHMe \cdot HCl$, slender needles, m. p. 130°). The second fraction is composed of *octa-acetyldisalicinmethylamine*, $NMe(CH_2 \cdot C_6H_4 \cdot O \cdot C_6H_7O_5Ac_4)_2$, colourless needles, m. p. $198-200^\circ$, $[\alpha]_D^{25} - 35.40^\circ$, $[\alpha]_D^{25} - 33.75^\circ$ when dissolved in chloroform, from which a uniform material could not be prepared by hydrolysis with acids.

Tetra-acetylsalicin bromide and ethylamine, under similar treatment, give *penta-acetylsalicinethylamine*, small, colourless needles, m. p. $96-97^\circ$, and *octa-acetyldisalicinethylamine*, long, colourless needles, m. p. $151-153^\circ$.

Tetra-acetylsalicin bromide is converted by diethylamine into *salicindiethylamine*, $C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot NEt_2$, small, colourless needles, m. p. $102-103^\circ$, $[\alpha]_D^{25} - 26.05^\circ$ in chloroform solution. With methylaniline in boiling methyl alcoholic solution, it gives *tetra-acetylsalicinphenylmethylamine*, long, colourless needles, m. p.

140–141°, $[\alpha]_D^{20} -19.78^\circ$ in chloroform, which is transformed by methyl alcoholic ammonia into *salicinphenylmethylaniline*, small crystals, $[\alpha]_D^{20} -36.23^\circ$ when dissolved in acetone.

Tetra-acetylsalicin bromide is converted by trimethylamine in absolute alcoholic solution into *tetra-acetylsalicintrimethylammonium bromide*, $C_8H_7O_5Ac_4 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot NMe_3Br$, colourless needles, m. p. 68° after softening at 65°, $[\alpha]_D^{20} -42.28^\circ$ in aqueous solution. It is hydrolysed by hydrochloric acid (5%) to *o-hydroxybenzyltrimethylammonium chloride*, slender needles ($+H_2O$), m. p. 96°; anhydrous, m. p. 200° (decomp.). H. W.

Saponins. VII. A. W. VAN DER HAAR (*Ber.*, 1922, 55, [B], 1054–1066; cf. this vol., i, 160).—It is shown that several saponins, such as hederagenin and others, are closely related to one another and to the terpene hydrocarbons (for example, sesquiterpenes) on the one hand and to phytosterols (sitosterol), cholesterol, and phytosterol-like substances (urson, oleanol) on the other. Hederagenin is decomposed by distillation with zinc dust in a current of hydrogen into sesquiterpenes, carbon dioxide, and water, in accordance with the equation $C_{30}H_{47}(OH)_2 \cdot CO_2H + H_2 = 2C_{15}H_{24} + CO_2 + 2H_2O$. The sesquiterpene volatile with steam which gives the violet coloration of saponins and saponins with sulphuric acid is to be regarded as the primary product of the distillation of hederagenin with zinc dust. During the process it undergoes partial conversion into terpene hydrocarbons which are not volatile with steam; the violet glacial acetic-sulphuric acid reaction passes to bluish-green. The volatile sesquiterpenes consist of a mixture of structurally different sesquiterpenes. The distillation of hederagenin with zinc dust in an atmosphere of hydrogen is most conveniently effected rapidly from a small retort heated on a sand-bath. H. W.

The Optical Activity of Catechins. K. FEIST and A. FUTTERMENGER (*Ber.*, 1922, 55, [B], 942–944; cf. Feist and Schön, A., 1921, i, 117; Freudenberg, A., 1921, i, 576, 577).—The observation of the optical activity of catechins in water, alcohol, or aqueous acetone is rendered very difficult by the inability to use any but very dilute solutions. Exact values can only be obtained when the hydroxyl groups of the catechin are protected by esterification or etherification. H. W.

Preparation of Coumarins. WOLFGANG FONSDORF (D.R.-P. 338737; from *Chem. Zentr.*, 1921, iv, 1224–1225).—Phenols or phenol ethers are condensed with fumaric or malic acids or their derivatives at temperatures above 120°. In the condensation of fumaric acid with phenols, the ortho-hydrogen atom of the phenol unites with a carboxyl group of the acid, giving formic acid; ring closure and formation of coumarin follows the elimination of water from the coumaric acid thus formed. Zinc chloride or, preferably, 73% aqueous or alcoholic sulphuric acid may be used as condensing agents. By condensation of *p*-cresol with fumaric acid

in the presence of sulphuric acid at 130–180° 6-methylcoumarin, m. p. 72–73°, is formed. G. W. R.

Dyes Containing the Furan Ring. R. R. KENSHAW and NELLIE M. NAYLOR (*J. Amer. Chem. Soc.*, 1922, **44**, 862–864).—The authors have repeated the work of Fisher (cf. A., 1878, 51) on the furan analogue of malachite-green. Contrary to the results of Fisher, they find that the product obtained by the oxidation of tetramethyldiaminodiphenylfurylmethane has a deeper colour than malachite-green and that it is an equally stable dye, giving handsome effects on silk and wool. Its oxalate and its zincchloride were prepared.

Pyromucic acid was condensed with pyrogallol, giving a yellowish-brown powder, m. p. 160°, which is presumably the furan analogue of alizarin-yellow-A. It gives a dark tan colour on cotton mordanted with turkey-red. W. G.

The System Furfuraldehyde-Water. GERALD H. MAINS (*Chem. and Met. Eng.*, 1922, **26**, 779–784, 841–843).—The corrected boiling point of pure furfuraldehyde is 161.7° at 760 mm., and d_4^{20} 1.1598 or d_4^{25} 1.1545, both values corrected to vacuum. The composition-specific gravity tables for solutions of furfuraldehyde in water up to the saturation concentration were determined at 20° and 25°, and were subsequently used as a method of analysis, accurate to $\pm 0.02\%$, in the determination of the mutual solubility and boiling-point and condensation-point curves for the system furfuraldehyde-water. The solubility of furfuraldehyde in water rises from 8.12% at 16° to 8.72% at 27° and 17% at 92°, whilst that of water in furfuraldehyde rises from 3.5% at 8° to 5.4% at 26.5° and 15.5% at 96°. The most important data emerging from the boiling-point curves of furfuraldehyde-water mixtures are as follows. With increasing amount of furfuraldehyde in the solution the boiling point gradually falls from 100° to a minimum of 97.9°, which is reached at the composition 18.4% furfuraldehyde, at which point two layers commence to be formed. Through the whole of this range the vapour phase contains a much higher percentage of furfuraldehyde than the liquid, rising to 35% at the minimum boiling point. From this point during the whole range in which there are two liquid layers, that is, up to 84% of furfuraldehyde, the boiling point and composition of the vapour phase remain constant. With higher concentrations than 84%, the boiling point rapidly rises until at 161.7° pure furfuraldehyde only remains. From the above data it is evident that by taking advantage of the great divergence in the boiling-point and condensation-point curves in this system, it is possible to effect readily a separation of furfuraldehyde from dilute aqueous solutions by fractional distillation, whereby a fraction containing furfuraldehyde and water in two layers boiling at 97.9–100° first distils. The aqueous furfuraldehyde layer is separated and the residual aqueous layer returned to the still. The aqueous high percentage furfuraldehyde is then dried by redistillation, water passing over first

and then furfuraldehyde of constant boiling point. In conclusion, the mathematical relations for the distillation of mixtures, as developed by Lord Rayleigh, are discussed with reference to the furfuraldehyde-water system.

G. F. M.

Preparation of Thionaphthencarboxylic Acids. GESELLSCHAFT FÜR TEERVERWERTUNG M. B. H., RUDOLF WEISSGERBER UND OTTO KRUBER (D.R.-P. 341837; from *Chem. Zentr.*, 1921, iv, 1225).—Sodium thionaphthen is treated with carbon dioxide in the absence of water, and the carboxylic acids thus obtained are separated by their varying acidities or by the fractionation of their esters. For example, anhydrous thionaphthen is treated with sodamide at 140–150° for five hours in a shaking vessel. A stream of dry carbon dioxide is then passed without lowering the temperature or interrupting the shaking. By treatment of the cooled products of reaction with water and toluene, the sodium salts are obtained in aqueous solution and the unchanged thionaphthen in toluene solution. The thionaphthencarboxylic acids are liberated by acidifying. By dissolving in sodium carbonate solution and partial acidification, the more strongly acid, *thionaphthen-2:3-dicarboxylic acid* is separated from the weaker acid, *thionaphthen-2-carboxylic acid*. The acids may also be separated by fractionation of their methyl esters (Weissgerber and Kruber, A., 1920, i, 754). *Methyl thionaphthen-2-carboxylate* has b. p. 176–180°/13 mm. *Methyl thionaphthen-2:3-dicarboxylate* has b. p. 214–218°/13 mm.

G. W. R.

Space Structural Formulæ of Chemical Substances in General, and of some Alkaloids in Particular. J. J. LYNST ZWIKKER (*Chem. Weckblad*, 1922, 19, 158–162).—Asymmetric as well as symmetric molecules may be regarded as harmonious groupings of atoms in space, building up constellations of simple and regular form.

In the cases of the alkaloids cinchonine, quinine, berberine, hydrastinine, and narceine, this form is the trigonal bipyramid, the 18 carbon atoms being regularly spaced in pairs along the nine edges. It is probable that the simplest and most stable form of this constellation is represented by the hydrocarbon retene.

S. I. L.

The Anhalonium [Cactus] Alkaloids. III. The Constitution of Anhaline. ERNST SPÄTH (*Monatsh.*, 1921, 42, 263–266).—The identity of anhaline with hordenine (A., 1919, i, 548) has been confirmed by a direct comparison of the two bases and of a number of their derivatives. The picrate has m. p. 139–140°, the picrolonate, m. p. 219–220°, the quaternary ammonium compound with methyl iodide, m. p. 230–231°, and the hydriodide of the acetylated base, m. p. 176–177°.

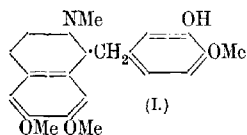
E. H. R.

Preparation of Tropinonecarboxylic Acid Esters. E. MERCK and OTTO WOLFES (Brit. Pat. 153917).—Ethyl tropinonecarboxylate is obtained by the condensation of succinaldehyde, methylamine, and ethyl acetoacetate (cf. T., 1917, 111, 762). A

mixture of 8.6 parts of succinaldehyde, an alcoholic solution of 10 parts of methylamine, and 13 parts of acetoacetic ester dissolved in 30 parts of alcohol is kept for three days, the product is neutralised, freed from alcohol, rendered alkaline with aqueous potassium carbonate solution, and extracted with chloroform. The tropinone-carboxylic ester is then transferred to dilute sulphuric acid solution, and back to chloroform, and finally the chloroform is distilled, leaving the ester as an oil which gradually solidifies on keeping in contact with the air. G. F. M.

Preparation of Tropinonecarboxylic Acid Esters. E. MERCK, OTTO WOLFES, and HORST MAEDER (Brit. Pat. 164757).—Ethyl tropinonecarboxylate is obtained by the hydrolysis of one ester group in diethyl tropinonedicarboxylate (cf. T., 1917, 111, 762) and simultaneous elimination of carbon dioxide. Twenty-eight parts of the diethyl ester in 50 parts of alcohol are heated to boiling with 22 parts of potassium hydroxide solution (1:1). After cooling, ice is added, the liquid is acidified with sulphuric acid, supersaturated with ammonia, and extracted with ether or a chlorinated hydrocarbon. Ethyl tropinonecarboxylate is an oil forming a crystalline hydrate, m. p. 63°. G. F. M.

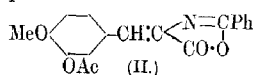
The Synthesis of Laudanine. ERNST SPÄTH and NORBERT LANG (*Monatsh.*, 1921, 42, 273—285).—Laudanine was shown by Späth (A., 1921, i, 50) to have the annexed formula (I). This



has now been confirmed by synthesis of the alkaloid. The synthesis depended on the known method of preparing isoquinoline derivatives by effecting ring-closure in *N*-acyl derivatives of ω -phenylethylamine. Homoveratrylamine, β -aminooctyl-3:4-di-

methoxybenzene was prepared by Rosenmund's method (A., 1911, i, 34) by condensing 3:4-dimethoxybenzaldehyde with nitromethane, followed by reduction of the ω -nitrostyrene in two stages.

3-Hydroxy-4-methoxyphenylacetic acid (homoisovanillic acid) is prepared by condensing isovanillin with hippuric acid in presence of sodium acetate and acetic anhydride, whereby the

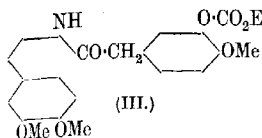


lactone of α -benzoylamino-3-acetoxy-4-methoxycinnamic acid (II) is formed, yellow needles from alcohol, m. p. 134—136°. When this is

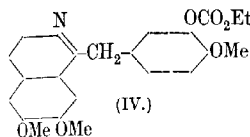
warmed with 15% sodium hydroxide solution, the acetyl group is removed and the lactone ring opened. The resulting α -benzoylamino-3-hydroxy-4-methoxycinnamic acid forms colourless crystals, m. p. 213.5—215.5° (decomp.). When the lactone is boiled with 23.5% potassium hydroxide, the desired 3-hydroxy-4-methoxyphenylpyruvic acid is obtained, along with resinous products. This compound forms a voluminous precipitate when light petroleum is added to its ethereal solutions; it has m. p. 183—184.5° (decomp.), and decomposes gradually on exposure to air. The ethylcarbonato-derivative, in which the hydroxyl group is replaced by the ethyl-

carbonato-group, is crystalline, m. p. 143–146°. By oxidation of its sodium salt in aqueous solution with hydrogen peroxide, 3-hydroxy-4-methoxyphenylpyruvic acid was converted into 3-hydroxy-4-methoxyphenylacetic acid in 80–90% yield; the product forms long needles from ether, m. p. 122.5–124.5°. For condensation with homoveratrylamine, it was converted into its *ethylcarbonato-derivative*, m. p. 112–113°.

The 3-ethylcarbonato-4-methoxyphenylpyruvic acid was converted into the acid chloride and the crude product condensed in benzene solution with the above β -aminoethyl-3:4-dimethoxybenzene. The product (III) could not be purified, but was treated directly with phosphoric oxide in toluene



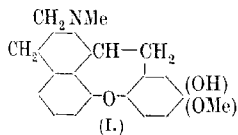
solution. From the products of the reaction was isolated 1-[ethylcarbonatoisovanillyl]-6:7-dimethoxy-3:4-dihydroisoquinoline (IV), which forms a crystalline *hydrochloride*, m. p. 193.5° (decomp.). The base was converted into the methylisoquinolinium iodide, which could not be obtained pure, and thence into



the corresponding *chloride*, which forms a well-characterised, yellow, crystalline double salt with platinum chloride. The methylisoquinolinium chloride was reduced with tin and hydrochloric acid, giving a mixture of laudanine and its ethylcarbonato-derivative, not all of which was hydrolysed during the reduction. The laudanine was proved to be identical with natural laudanine. E. H. R.

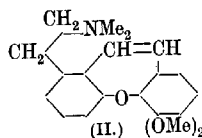
Alkaloids of the Pareira Root. II. isoChondodendrine. FRANZ FALTIS and FELIX NEUMANN (*Monatsh.*, 1921, 42, 311–376; cf. Faltis, A., 1912, i, 796; Scholtz, A., 1913, i, 87, 385; 1915, i, 450).—A long historical account is given of the alkaloids of the pareira root, which have been known as bebeerines. It is shown that these alkaloids are different from that obtained from the bark of *Nectandra Rodiari*, the so-called bebeerin tree, and that the true source of pareira root is *Chondodendron platyphyllum*. For this reason, it is proposed to substitute the names α -, β -, and isobeeberine, respectively.

isoChondodendrine (and probably α - and β -chondodendrine) has the composition $C_{18}H_{19}NO_3$, which has been resolved into $OH \cdot C_{16}H_{12}ONMe \cdot OMe$. Starting from the hypothesis that iso-

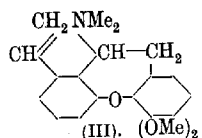


chondodendrine is related to laudanone, it may have the following configuration (attached formula, I). Methylation in the hydroxyl group, without formation of a quaternary ammonium compound, was only accomplished with diazomethane. *Methyl-*

isochondodendrine forms a crystalline crust, m. p. 256–257°, $[\alpha]_D^{20}$ –36.8° in alcohol. Its methiodide has $[\alpha]_D^{20}$ –7° in 50% alcohol. De-

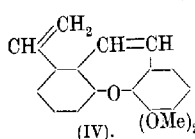


m. p. 204–205°. It forms tabular, triclinic crystals [$a : b : c = 1.6996 : 1 : 1.2908$; $\alpha = 91^\circ 5\frac{1}{2}'$; $\beta = 103^\circ 27'$; $\gamma = 91^\circ 20'$]. The



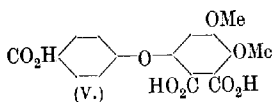
β -methine (III), m. p. 167–168.5°, has $[\alpha]_D^{20} +35.3^\circ$ in pyridine, +359° in alcohol. With sulphuric acid, the α -methine gives a deep red solution on warming, suddenly changing to blue. Scholz attributed this reaction to the active β -methine, which does not show it. The α -methine by reduction with sodium and alcohol gave the α -dihydromethine, m. p. 211.5–212°, which was also obtained by reduction of methylisochondodendrine methochloride with sodium amalgam. It forms small tetragonal crystals [$a : c = 1 : 0.38257$]. Its hydrochloride forms a double chloride with gold chloride, $C_{20}H_{25}O_3N, HAuCl_4$.

By reduction of the methiodides of the mixed α - and β -methines with powdered sodium hydroxide in methyl alcohol, a nitrogen-free compound, $C_{18}H_{16}O_3$, containing two ethylene linkings, was obtained; tabular six-sided monoclinic crystals [$a : b : c = 0.8271 : 1 : 0.8416$; $\beta = 99^\circ 35'$]; it does not melt below 312°. The



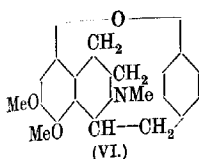
formula IV is suggested. Reduction of the α -dihydromethine gave a similar compound, $C_{18}H_{18}O_3$, containing only one double bond. This has no m. p. and forms tabular, monoclinic crystals [$a : b : c = 0.8470 : 1 : 0.6160$; $\beta = 97^\circ 45\frac{1}{2}'$]. The constitution suggested is that of IV with the –CH:CH– bridge reduced.

Oxidation of the compound $C_{18}H_{16}O_3$ with potassium permanganate gave a tricarboxylic acid, $C_{12}H_5O(OMe)_2(CO_2H)_3$, m. p. 177.5–178°, which forms an *anhydride*, m. p. 244–245°, and a *trimethyl ester*, m. p. 100–102°. Demethylation of the tricarboxylic acid gave a dihydroxydicarboxylic acid showing the colour reactions of catechol, and therefore having the two hydroxyl groups in the ortho-position to each other. By fusion with potassium hydroxide, the tricarboxylic acid gave a good yield of *p*-hydroxybenzoic acid, and after methylation of the residue a trimethoxybenzoic acid,



m. p. 141–143°, was isolated, which appears to be the hitherto unknown 2:3:5-trimethoxybenzoic acid. In all probability, therefore, the above tricarboxylic acid has formula V. This

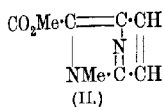
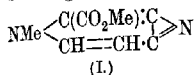
leads unexpectedly to the formula (VI) for methylisochondodendrine,



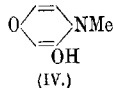
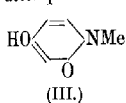
in which the oxygen bridge is in an unusual position. It had been expected that the oxygen bridge would be as in formula I, but if this were the case, salicylic acid should have been obtained instead of *p*-hydroxybenzoic acid in the above potassium hydroxide fusion. Attempts to detect isomeric change of salicylic acid into *p*-hydroxybenzoic acid under similar experimental conditions gave negative results. Confirmation of the formula was obtained by distilling isochondodendrine with zinc dust when *p*-cresol was obtained. The formula of isochondodendrine will be similar to VI with (OH) in place of one of the (OMe) groups, but there is no evidence to show which.

E. H. R.

The Constitution of Ricinine. ERNST SPÄTH and ERICH TSCHERNITZ (*Monatsh.*, 1921, 42, 251—262).—Ricine has generally been regarded as the methyl ester of ricinic acid, and different formulæ have been proposed for it, (I) by



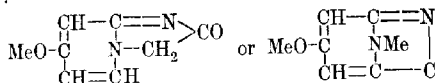
Philippe by heating ricinic acid with hydrochloric acid, has been attempted and successfully accomplished. The latter compound is



shown to be identical with a pyridone of formula (III) or (IV), whilst the compound $\text{C}_7\text{H}_9\text{O}_2\text{N}$ is the *O*-methyl derivative of either III or IV. The synthesis was accomplished as follows. 2:4-Dihydroxypyridine was converted into the corresponding dimethoxy-derivative by treating its silver salt with methyl iodide in ethereal solution. The dimethyl ether was characterised by the preparation of its picrolonate, m. p. 148—149°. By further treatment of this compound with methyl iodide, it was converted directly into 4-methoxy-1-methyl-1:2-dihydropyrid-2-one or 2-methoxy-1-methyl-1:4-dihydropyrid-4-one identical with the ricinine derivative, $\text{C}_7\text{H}_9\text{O}_2\text{N}$, m. p. 113—114°. It forms a picrate, long, yellow, felted needles, m. p. 154—155°, and a picrolonate, golden-yellow crystals, m. p. 126.5° (decomp.). When heated with fuming hydrochloric acid at 140° in a sealed tube, the compound is demethylated, forming a compound, $\text{C}_6\text{H}_7\text{O}_2\text{N}$, identical with that obtained by Maquenne and Philippe from ricinic acid. A comparison of the boiling point of the compound $\text{C}_7\text{H}_9\text{O}_2\text{N}$, 161—162°/16 mm., with those of 1-methyl-1:2-dihydropyrid-2-one, 126.5°/14.5 mm., and of the corresponding pyrid-4-one, 223—224°/15 mm., leads to the

conclusion that the compounds under consideration correspond with formula (III) rather than (IV).

The methyl groups of ricinine being thus accounted for in the decomposition product $C_7H_9O_2N$, it follows that ricinine cannot be, as hitherto supposed, the methyl ester of a carboxylic acid, and the formulæ hitherto proposed must be rejected. The ease of hydrolysis of the methoxyl group may be accounted for by fusion of the pyridine ring with another ring, in all probability a glyoxaline ring, as suggested by Böttcher. These and other properties of ricinine may be summarised in either of the two formulæ :

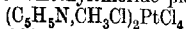


E. H. R.

Taxine, the Alkaloid from the Yew, *Taxus baccata*. I. E. WINTERSTEIN and D. IATRIDES (*Z. physiol. Chem.*, 1921, 117, 240—283).—Taxine, obtained in yield of 0.7—1.4% from dried yew-needles, has the formula $C_{37}H_{51}O_{10}N$. It has not been possible to obtain it or its salts in a crystalline condition. The amorphous base sinters at 97° and melts at 105—110°, $[\alpha]_D +53.15^\circ$ in 1% sulphuric acid, $+51.52^\circ$ in absolute alcohol. With dilute organic and inorganic acids, cinnamic acid, acetic acid, a substance having reducing properties, and a resinous product are formed. With sodium hydroxide in the cold, cinnamic acid is produced in small amounts. When heated by itself, taxine gives rise to a product containing nitrogen. On reduction, it unites with two molecules of hydrogen, forming a compound, $C_{37}H_{55}O_{10}N$; thus indicating the presence of two double bonds. Similarly, a yellow, amorphous compound, $C_{37}H_{51}O_{10}NBr_4$, m. p. 125—130° (decomp.), is formed on bromination. Acetic anhydride produces an acetyl derivative of uncertain constitution, which with alcoholic potassium hydroxide yields a molecular proportion of cinnamic acid. Methyl iodide gives a white *methiodide*, $C_{37}H_{51}O_{10}N.CH_3I$, m. p. 122—125°, which with alkali hydroxide yields a white, flocculent product, $C_{37}H_{48}O_{10}$, m. p. 120—140°, methylamine being eliminated. Oxidation with hydrogen peroxide results in the formation of a reducing compound which with phloroglucinol and hydrogen chloride gives a crystalline compound, light brown needles, m. p. 123°. With potassium permanganate, benzamide, benzoic acid, acetic acid, oxalic acid, and benzonitrile are formed and also a substance which with phenylhydrazine yields a compound, $(C_4H_6ON)_2$, white, glistening scales, m. p. 185°. W. O. K.

Additive Compounds of s.-Trinitroanisole with Tertiary Bases. M. GIUA (*Gazzetta*, 1922, 52, i, 182; cf. A., 1921, i, 592; Kohn and Grauer, A., 1914, i, 83; 1915, i, 836; Walthier, A., 1915, i, 836, 993).—When treated with alcoholic platinum

chloride solution, the additive compound of *s*.-trinitroanisole with pyridine yields pyridinemethylchloride platinichloride,

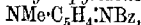


(cf. Bally, A., 1888, 964).

T. H. P.

Pyridinium Salts derived from some Chloroacetylaminocompounds. EDWARD DE BARRY BARNETT and JAMES WILFRED COOK (T., 1922, 121, 792—797).

The Products of the Benzoylation of 2-Aminopyridine. A. E. TSCHITSCHIBABIN and J. S. BYLINKIN (*Ber.*, 1922, 55, [B], 998—1002).—The action of benzoyl chloride or benzoic anhydride on 2-aminopyridine under very varied conditions leads to the production of a mixture of dibenzoylaminopyridine, slender needles, m. p. 166—167°, and 2-benzoylaminopyridine, $\text{C}_6\text{H}_5\text{N} \cdot \text{NHBz}$, large, colourless needles, m. p. 87° (*platinichloride*, orange-coloured needles, m. p. 230° [decomp.], *picrate*, yellow needles, m. p. 193°). The constitution of the substance is deduced from the observation that it is converted by the successive action of methyl iodide and alkali hydroxide into 1-methyl-2-pyridone-2-benzoylimide,



golden-yellow, granular crystals, m. p. 70° (*picrate*, small, yellow prisms, m. p. 157°), which is identical with the product obtained by the direct benzoylation of 1-methyl-2-pyridoneimide (A., 1921, i, 450). Dibenzoyl- α -aminopyridine appears to be identical with the substance described as benzoylaminopyridine by Marckwald. It is almost devoid of basic properties, and is characterised by the ease with which it loses a benzoyl group and passes into benzoylaminopyridine, m. p. 87°. When treated with platinum chloride in concentrated aqueous hydrochloric acid solution, it yields the platinichloride of the monobenzoyl derivative. It is not possible at present to decide between the alternative formulæ $\text{C}_6\text{H}_5\text{N} \cdot \text{NBz}_2$ and $\text{NBz} \cdot \text{C}_5\text{H}_4 \cdot \text{NBz}$.

H. W.

4:6-Diphenyl-2-methylpyridine. C. GASTALDI (*Gazzetta*, 1922, 52, i, 169—175; cf. this vol., i, 367).—The author has investigated the interaction of acetophenone and acetic anhydride in presence of sublimed ferric chloride, the product of which is regarded by Dilthey (A., 1916, i, 829) as a ferric chloride compound of 2:6-diphenyl-4-methylpyrylium chloride of the constitution

$$\text{FeCl}_4 \cdot \text{O} \begin{array}{c} \text{CPh} \cdot \text{CH} \\ \text{CMe} \cdot \text{CH} \end{array} \text{CPh}.$$

The author considers that this reaction is analogous to that occurring between dyponone and benzoyl chloride in presence of sublimed aluminium chloride with formation of 2:4:6-triphenylpyrylium chloride, and that the acetic anhydride, acting as a condensing agent, first converts the acetophenone into dyponone. This view is supported by the fact that the action of acetic anhydride on dyponone yields the ferric chloride compound of 4:6-diphenyl-2-methylpyrylium chloride. The constitution attributed to this compound by Dilthey is, therefore, erroneous, the mistake being the result of an earlier one made by von Meyer

and Irmischer (A., 1908, i, 911), who wrongly described as 4:6-diphenyl-2-methylpyridine, a compound of another structure. Thus the action of ammonia on the pyrylium salt obtained from either acetophenone or dynone by the action of acetic anhydride yields 4:6-diphenyl-2-methylpyridine, m. p. 185°, which Dilthey regarded as 2:6-diphenyl-4-methylpyridine. Further, the compound which Dilthey considered to be the ferric chloride compound of 2:6-di-*p*-anisyl-4-methylpyrylium chloride is probably the corresponding compound of 4:6-di-*p*-anisyl-2-methylpyrylium chloride.

4:6-Diphenylpyridine-2-carboxylic acid, $N \left\langle \begin{array}{c} C(CO_2H) \cdot CH \\ CPh = CH \end{array} \right\rangle CPh$, obtained by the action of potassium permanganate on 4:6-diphenyl-2-methylpyridine in presence of acid, crystallises in colourless needles, m. p. 150°; when the sodium salt is heated in a vacuum with the calcium oxide, it yields 2:4-diphenylpyridine, which forms a dense, pale yellow liquid, and gives the hydrogen sulphate, $C_{17}H_{15}N, H_2SO_4$, needles, m. p. 245° (slight browning). T. H. P.

2-*p*-Dimethylaminostyrylpyridine Methiodide, a New Photographic Sensitiser. WILLIAM HOBSON MILLS and WILLIAM JACKSON POPE (T., 1922, 121, 946—947).

Preparation of Hydrogenated 2-Phenylquinoline-4-carboxylic Acid, its Homologues, and their Salts. FRITZ ZUCK-MAYER (D.R.-P. 342048; from *Chem. Zentr.*, 1921, iv, 1225—1226).—2-Phenylquinoline-4-carboxylic acid, or its derivatives containing alkyl or alkoxy in the quinoline group, are treated with reducing agents and the tetrahydroquinolinecarboxylic acids thus obtained are changed into their alkali or alkaline-earth salts. Acid, alkaline, or electrochemical reducing agents may be used. The resulting phenyltetrahydroquinolinecarboxylic acids are more soluble in dilute acids than their parent compounds and form slightly soluble nitroso-derivatives. They can be acetylated. The reduction of 2-phenylquinoline-4-carboxylic acid, either by iron and hydrochloric acid, by sodium amalgam, or electrochemically in alkaline solution, gives 2-phenyltetrahydroquinoline-4-carboxylic acid, white, felted needles, m. p. about 149°; lithium salt, white tasteless powder. Reduction of 8-methoxy-2-phenylquinoline-4-carboxylic acid by zinc and sodium hydroxide solution gives 8-methoxy-2-phenyltetrahydroquinoline-4-carboxylic acid; it crystallises in white needles, m. p. 185—186°. The acids and their salts have therapeutic uses as antipyretics and eliminators of uric acid. G. W. R.

Polynuclear Heterocyclic Aromatic Types. I. Some Indenoquinoline Derivatives. JAMES WILSON ARMIT and ROBERT ROBINSON (T., 1922, 121, 827—839).

Benzoxazole Derivatives. SIEGFRIED SKRAUP and MARIE MOSER (*Ber.*, 1922, 55, [B], 1080—1101; cf. Skraup, A., 1919, i, 598).—A description of attempts to prepare benzoxazolyl phenyl

ketone and a further account of the influence of substituents on the opening of the benzoxazole ring.

Attempts to prepare benzoxazyl phenyl ketone by converting 2-aminobenzoxazole into the corresponding nitrile and treatment of the latter with the requisite Grignard reagent were rendered unsuccessful by the apparent impossibility of diazotising the amino-substance.

Benzoxazole-2-carboxylic acid, colourless crystals, m. p. 85°, is obtained in small amount by the action of potassium permanganate on 2-methylbenzoxazole, but is more conveniently prepared by the oxidation of 2-*o*-hydroxyphenylbenzoxazole (long, pale pink needles, m. p. 123°, obtained by heating *o*-aminophenol with salicylamide); the potassium, silver, mercurous, mercuric, lead, and copper salts are described. The potassium salt is converted by thionyl chloride into *benzoxazole-2-carboxyl chloride*, m. p. 85°. The latter substance mainly suffers reduction when treated with magnesium phenyl bromide; in cold solution it is possible to obtain *benzoxazyl-diphenylcarbinol*, $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{N} \\ \text{O} \end{smallmatrix}\text{>C-Ph}_2\text{-OH}$, colourless crystals, m. p. 157°, in small amount, but the main product is 2-*hydroxymethylbenzoxazole*, $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{N} \\ \text{O} \end{smallmatrix}\text{>C-CH}_2\text{-OH}$, m. p. 125°, and this is formed exclusively when the action is carried out in warm solution. *Benzoxazole-2-carboxyanilide*, m. p. 156–157°, is reduced in a similar manner by magnesium methyl iodide with the formation of *benzoxazole-2-aldehydeanil*, $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{N} \\ \text{O} \end{smallmatrix}\text{>C-CH:NPh}$, m. p. 153°.

Greater success was met in a series of experiments which depend on the reactivity of the methylene hydrogen atoms of 2-benzylbenzoxazole. The latter is converted by *p*-nitrosodimethylaniline into the compound, $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{N} \\ \text{O} \end{smallmatrix}\text{>C-Ph:N-C}_6\text{H}_4\text{-NMe}_2$, slender, lustrous needles, incipient decomp. 150°, by 2:4-dinitrophenyldiazonium sulphate into the substance, $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{N} \\ \text{O} \end{smallmatrix}\text{>C-Ph:N-NH-C}_6\text{H}_3(\text{NO}_2)_2$, yellow crystals, m. p. 140°, and by amyl nitrite and sodium ethoxide into *benzoxazyl phenyl ketoxime*, m. p. 193°. The latter substance is converted by absolutely anhydrous acetic acid at 190° into the desired *benzoxazyl phenyl ketone*, but the reaction appears to be influenced to an unusual extent by the presence of traces of moisture.

2-Ethylbenzoxazole, from *o*-aminophenol and propionitrile at 205–210°, has b. p. 210°, d^{20}_4 1.081. 2-β-Naphthylbenzoxazole has m. p. 115–116°, 2-*p*-nitrophenylbenzoxazole, long needles, m. p. 260°, is obtained from *o*-aminophenol and *p*-nitrobenzonitrile at 135–140°; the preparation of the corresponding *m*- and *p*-nitro-compounds in this manner does not appear to be possible, but 2-*m*-nitrophenylbenzoxazole, m. p. 207°, is obtained from *o*-aminophenol and *m*-nitrobenzoyl chloride.

The velocity of hydrolysis of benzoxazole and its 2-substituted derivatives by hydrochloric acid (20.2%) has been measured at 61° and 108°. The reaction is apparently unimolecular, since

water is present in large excess; its velocity depends greatly on the substituent and gives a measure of the valency demands of the latter.

H. W.

Thiazoles. I. Derivatives of 2-Phenylbenzthiazole. Synthesis of an Analogue of Cinchophen (Atophan). MARSTON T. BOGERT and EMANUEL M. ABRAHAMSON (*J. Amer. Chem. Soc.*, 1922, **44**, 826—837).—The most satisfactory method of preparing 2-phenylbenzthiazole is by the fusion of benzanilide or benzylidene-aniline with sulphur. The product obtained by its nitration is shown to be the 6-nitro-derivative (cf. Nägeli, A., 1895, i, 347). When reduced, the nitro-derivative yields 6-amino-2-phenylbenzthiazole, giving an *acetyl* derivative, m. p. 214° (corr.). On fusion with potassium hydroxide, the amine gives benzoic acid and no aminobenzoic acid. Further, it couples only once with diazotised *p*-nitroaniline, giving *p*-nitrobenzeneazo-6-amino-2-phenylbenzthiazole, m. p. 196° (corr.), and its *acetyl* derivative, m. p. 203° (corr.). Finally, 6-aminophenylbenzthiazole gives a *benzylidene* derivative, m. p. 151° (corr.), which when fused with sulphur yields 2:2-diphenylbenzbisthiazole (cf. Green and Perkin, T., 1903, **83**, 1207). These facts establish the position of the amino- and consequently of the nitro-group. On nitration the bisthiazole yields 4-nitro-2:2-diphenylbenzbisthiazole, m. p. 262° (corr.), which on reduction gives 4-amino-2:2-diphenylbenzbisthiazole, m. p. 285—287° (corr.), giving an *acetyl* derivative, m. p. 250—253° (corr.). The positions of the nitro- and amino-groups in these compounds were established by the fact that, on fusion with potassium hydroxide, the amine did not give any aminobenzoic acid.

6-Amino-2-phenylbenzthiazole on methylation under pressure with methyl alcohol and hydrochloric acid gives 6-dimethylamino-2-phenylbenzthiazole, m. p. 185° (corr.), but no quaternary salt could be obtained. On bromination 2-phenylbenzthiazole gives a *tetrabromide*, m. p. 125° (decomp.), which when boiled with dilute acetic acid loses bromine and hydrogen bromide, yielding 6-bromo-2-phenylbenzthiazole, m. p. 152° (corr.), which was also obtained by the Sandmeyer reaction from 6-amino-2-phenylbenzthiazole. Similarly, by the Sandmeyer reaction 6-cyano-2-phenylbenzthiazole was prepared and this, on hydrolysis, yields 2-phenylbenzthiazole-6-carboxylic acid, m. p. 261—263° (corr. decomp.), giving a *methyl ester*, m. p. 153—154° (corr.). With iodine in acetic acid 2-phenylbenzthiazole gives a very unstable *di-iodide*, m. p. 84.5° (corr.). With *acetyl chloride* 2-phenylbenzthiazole gives an *additive compound*, which readily loses *acetyl chloride* again on warming or on shaking with water.

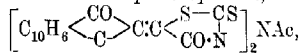
The 6-carboxylic acid mentioned above is structurally analogous to cinchophen (α -phenylcinchoninic acid), and it is hoped that it may show useful therapeutic properties.

W. G.

Rhodanine. II. CH. GRÄNACHER, H. REIS, and E. POOL (*Helv. Chim. Acta*, 1922, **5**, 382—391).—The red dye resulting from the oxidation of rhodanine by means of ferric chloride (A., 1920,

i, 252) is of the indigoid type. Thus the product obtained from *N*-phenylrhodanine was purified by conversion into a soluble reduction product by means of sodium hyposulphite, followed by oxidation with air. Analytical data, but no formula, are supplied for the magenta-like powder, with a green reflex, so prepared. It, and the following condensation products of rhodanines with α -diketones, are very easily converted by alkali into compounds only slightly coloured. *N*-Phenylrhodanine- α -acenaphthenequinone, $\text{Ph}\cdot\text{N}\cdot\text{CO}>\text{C}:\text{C}<\begin{smallmatrix} \text{CO} \\ \text{C}_{10}\text{H}_6 \end{smallmatrix}$, needles, yields a dinitro-

derivative, $\text{C}_{21}\text{H}_4\text{O}_2\text{NS}_2(\text{NO}_2)_2$, m. p. 342° (decomp.). Rhodanine- α -acenaphthenequinone, $\text{C}_{15}\text{H}_2\text{O}_2\text{NS}_2$, forms red needles. Imido-acetyldi-*N*:*N*-rhodanine- α -acenaphthenequinone,



forms scarlet leaflets. Iminodi-*N*:*N*-rhodanine- α -acenaphthenequinone, $\left[\text{C}_{10}\text{H}_6 < \begin{smallmatrix} \text{CO} \\ \text{C} \end{smallmatrix} > \text{C}:\text{C} < \begin{smallmatrix} \text{S}-\text{CS} \\ \text{CO}\cdot\text{N} \end{smallmatrix} \right]_2 \text{NH}$, crystallises in dark red needles.

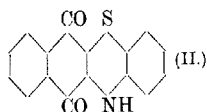
α -Oximino-*N*-phenylrhodanine, $\text{C}_6\text{H}_5\text{O}_2\text{N}_2\text{S}_2$, forms golden-yellow needles, m. p. 181° ; its silver salt exists in two forms, respectively yellowish-brown and reddish-orange; ethyl ether, $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_2\text{S}_2$, is yellowish-orange, m. p. 130° . α -Nitro-*N*-phenylrhodanine, $\text{Ph}\cdot\text{N}\cdot\text{CO}>\text{CH}\cdot\text{NO}_2$, from the preceding oximino-compound and nitric acid, forms light yellow needles, m. p. 207° (decomp.).

α -Oximino-*N*-phenylthiohydantoin, $\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{CS}-\text{S} \end{smallmatrix} > \text{C}:\text{NOH}$, forms yellow needles, m. p. $151-153^\circ$; the silver salt exists in two forms. Reduction of the oximino-compound with zinc dust and acetic acid would seem to yield a rhodanine-purpuric acid (cf. Knorr, *Annalen*, 1887, **238**, 192). α -Oximino-*N*-phenylthiohydantoin, $\begin{smallmatrix} \text{Ph}\cdot\text{N}\cdot\text{CO} \\ \text{HN}:\text{C}-\text{S} \end{smallmatrix} > \text{C}:\text{NOH}$, forms yellow needles, m. p. $199-200^\circ$. J. K.

Linear Benzonaphthaparathiazine [$\beta\beta$ -Naphthaphenthiazine]. K. FRIES and F. KERKOW (*Annalen*, 1922, **427**, 281-302; cf. Kehrman and Christopoulos, A., 1921, i, 449; Ludwig-Semelci, 1921, i, 448, 689).

—This (I) is the only one of the three possible naphthaphenthiazines which has not previously been prepared. Its preparation is now described and general methods for obtaining its substitution products are indicated.

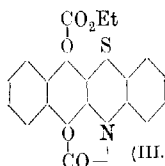
3-Chloro-2-anilino-1:4-naphthaquinone (prepared from 2:3-dichloronaphthaquinone and aniline) reacts with sodium sulphide, giving 2-anilino-3-mercapto-1:4-naphthaquinone, which is characterised by an *S*-methyl derivative, m. p. 143° . The mercaptan undergoes oxidation when air is led through a boiling alcoholic



solution, and gives $\beta\beta$ -naphthaphenthiazine-6:11-quinone (II), which forms steel-blue crystals, m. p. 308° . On further oxidation by means of hydrogen peroxide, this substance yields a *sulphoxide*, an amphoteric substance melting above 360° , and a *sulphone*, an

orange-red, acidic compound, which also melts above 360° .

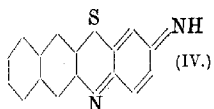
12-Methyl- $\beta\beta$ -naphthaphenthiazine-6:11-quinone, reddish-blue needles, m. p. 197° , is prepared by directly methylating the thiazine (II) with methyl sulphate in the presence of magnesium oxide. Halogen derivatives of the thiazine containing the halogen atom in the 3-position are prepared by isomeric change of the halogen salts of the sulphoxide. 3-Chloro- $\beta\beta$ -naphthaphenthiazine-6:11-quinone forms small, stout, blue needles, m. p. 303° , and 3-bromo- $\beta\beta$ -naphthaphenthiazine-6:11-quinone, steel-blue needles, m. p. 309° . 6:11-Dihydroxy- $\beta\beta$ -naphthaphenthiazine, small, colourless crystals,



m. p. 192° (diacetyl derivative, m. p. 258° ; dimethyl ether, m. p. 134°), is obtained by reducing the quinone with stannous chloride and acetic acid or with alkaline hyposulphite; atmospheric oxidation reconverts it into the quinone. The action of ethyl chloroformate on the sodium salt of the quinol gives rise to the 11:12-lactam of ethyl $\beta\beta$ -naphthaphenthiazine-6:11-dicarboxylate (III), which forms greenish-yellow needles, m. p. 203° (decomp.). Complete reduction of the quinone with stannous chloride yields $\beta\beta$ -naphthaphenthiazine, yellow needles, m. p. 277° .

A corresponding series of compounds containing an amino- or acetylamino-group in position 3 is described; these substances are obtained by a similar series of reactions starting from 2:3-dichloronaphthaquinone and *p*-phenylenediamine (or monoacetyl-*p*-phenylenediamine) instead of from 2:3-dichloronaphthaquinone and aniline. 3-Chloro-2-*p*-aminoanilino-1:4-naphthaquinone forms bluish-violet crystals, m. p. above 360° . 3-Chloro-2-*p*-acetylamino-anilino-1:4-naphthaquinone forms small, purplish-red crystals, m. p. 271° (decomp.). 2-*p*-Acetylamino-3-mercapto-1:4-naphthaquinone gives a *S*-methyl ether, m. p. 243° . 3-Acetylamino- $\beta\beta$ -naphthaphenthiazine-6:11-quinone forms green needles which decompose above 290° (sulphoxide, m. p. 330° , decomp., sulphone, m. p. above 360°). 3-Amino- $\beta\beta$ -naphthaphenthiazine-3:10-quinone sinters at 240° , m. p. 290° (decomp.). 3-Acetylamino-6:11-dihydroxy- $\beta\beta$ -naphthaphenthiazine is characterised by its green hydrochloride, and by acetylation to 3-acetylamino-6:11-diacetoxy- $\beta\beta$ -naphthaphenthiazine, m. p. 257° (decomp.). 3-Amino- $\beta\beta$ -naphthaphenthiazine is a yellow powder, m. p. 280° (decomp.) [hydrochloride is pale olive-green; the acetyl derivative forms greenish-yellow crystals, m. p. 285° (decomp.)].

When a current of air is passed through a boiling solution of 3-amino- $\beta\beta$ -naphthaphenthiazine oxidation occurs and the 3-



imino-compound (IV) is precipitated. It forms small, dark blue crystals, m. p. 290° (decomp.), and on warming with alkaline hyposulphite passes back into the aminothiazine. C. K. I.

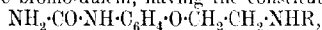
Preparation of Intermediate Products and Colouring Matters. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Fr. Pat. 521281; from *Chem. Zentr.*, 1921, iv, 1271—1272).—Monoacyl derivatives are prepared from diaminodiarlylsulphones, obtained from *m*-phenylenediamine, by treatment with acylating agents. *Monoacetyl-2:5-diaminophenyl-1-p-tolylsulphone* is obtained from 2:5-diaminophenyl-*p*-tolylsulphone (D.R.-P. 282214) and acetic anhydride, ethyl acetate, or acetic acid; it forms crystals, m. p. 182—183°. Other derivatives are prepared similarly. *Mono-benzoyl-2:5-diaminophenyl-p-tolylsulphone* has m. p. 186°. *Monophthaloyl-2:5-diaminophenyl-p-tolylsulphone* is transformed by recrystallisation from acetic acid into the *anil*, m. p. 232°. *Monoacetyl-2:5-diaminophenyl-p-chlorophenylsulphone* has m. p. 198—199°. *Monophthaloyl-2:5-diaminophenyl-p-chlorophenylsulphone* gives an *anil*, m. p. 233°. *Monoacetyl-1:4-naphthylenediamine-2-p-toluene-6(7)-sulphonic acid* gives a colourless sodium salt. Colouring matters are obtained from their diazo-compounds and 2-naphthylamine or its derivatives, such as 2-amino-3-hydroxynaphthalene-6-sulphonic acid, 2-naphthylamine-6-sulphonic acid, etc.

G. W. R.

Preparation of Ethers of *p*-Hydroxyphenylcarbamide. J. D. RIEDEL, AKT.-GES. (D.R.-P. 339101; from *Chem. Zentr.*, 1921, iv, 1324).—The carbamides of *p*-aminophenol are converted into hydroxyalkyl ethers by the usual methods for the preparation of phenolic ethers. For example, *p-hydroxyphenyl-hydroxyethylcarbamide* is prepared from *p*-hydroxyphenylcarbamide, ethylene chlorohydrin, and sodium methoxide solution at 100°; *p-hydroxyphenyldihydroxyethylcarbamide* (spherical aggregates, m. p. 155—156°), from *p*-hydroxyphenylcarbamide, glycerol- α -monochlorohydrin, and sodium methoxide solution at 100—110°.

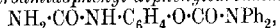
G. W. R.

Changes in the Sweetness of Dulcin (*p*-Phenetolecarbamide) caused by Chemical Alterations of the Molecule and the Sweetening Power of Derivatives of *p*-Hydroxyphenylcarbamide. CARL SPECKAN (*Ber. deut. pharm. Ges.*, 1922, 32, 83—107).—Replacement or substitution of the ethyl group of *p*-phenetolecarbamide led to the complete suppression of the sweet taste of this substance in every case investigated with the exception of β -bromo-*p*-phenetolecarbamide, which was also very sweet, and benzoyl-*p*-hydroxyphenylcarbamide which had a faintly sweet after-taste. Aromatic amino-derivatives prepared from the above bromo-dulcin, having the constitution



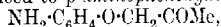
were quite tasteless, whilst the complete replacement of the ethyl

group by such groups as $-\text{CO}_2\text{Et}$, $-\text{CO}\cdot\text{NPh}_2$, etc., as also replacement of the end methyl group by acetyl or phenyl, likewise gave substances in which the sweet taste of dulcin was entirely suppressed. The preparation of the following substances is described. β -Bromo-*p*-phenetolecarbamide, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Br}$, from *p*-hydroxyphenylcarbamide and ethylene dibromide, white needles, m. p. $162-164^\circ$. Ethylene dicarbamidophenyl ether, $\text{C}_6\text{H}_4(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CONH}_2)_2$, a by-product of the above preparation, forms pale red needles, m. p. 342° . β -Anilino-*p*-phenetolecarbamide, from the β -bromo-derivative and aniline, forms fine, white needles, m. p. 230° . β -*p*-Phenetidino-*p*-phenetolecarbamide, has m. p. 215° . β -*p*-Toluidino-*p*-phenetolecarbamide, has m. p. 180° . β -*o*-Toluidino-*p*-phenetolecarbamide, has m. p. $228-230^\circ$. β -*m*-Toluidino-*p*-phenetolecarbamide, has m. p. 215° . β -*m*-Xylidino-*p*-phenetolecarbamide, has m. p. 255° . *p*-Carbamidophenyl ethyl carbonate, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{OEt}$, from *p*-hydroxyphenylcarbamide, sodium ethoxide and ethyl chloroformate, forms white needles, m. p. 158° . *p*-Carbamidophenyl diphenylcarbamate,

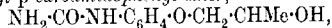


forms white crystals, m. p. 240° . Ethyl α -*p*-carbamidophenoxybutyrate, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$, from *p*-hydroxyphenylcarbamide and ethyl α -bromobutyrate in presence of potassium hydrogen carbonate, forms white crystals, m. p. 90° . *p*-Carbamidophenylglycid ether, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}$, from

p-hydroxyphenylcarbamide and epichlorohydrin in presence of sodium ethoxide, has m. p. 235° . Benzoyl-*p*-hydroxyphenylcarbamide and benzoyl-*p*-hydroxyphenylbenzoylcarbamide were both obtained by the action of benzoyl chloride on hydroxyphenylcarbamide, and have m. p. 148° and $226-228^\circ$, respectively. *p*-Carbamidophenoxyacetophenone, formed by the action of ω -bromoacetophenone on hydroxyphenylcarbamide and sodium ethoxide, has m. p. 140° . *p*-Nitrophenoxyacetone, prepared by the action of chloroacetone on *p*-nitrophenol in presence of sodium amyloxide, has m. p. 82° , and gives a semicarbazone, m. p. 225° , a phenylhydrazone, m. p. 155° , and an oxime, m. p. 105° . On catalytic hydrogenation, it was reduced to *p*-aminophenoxyacetone,



white leaflets, m. p. 236° , and this, on treatment with hydrochloric acid and potassium cyanate, gave *p*-carbamidophenoxyacetone, m. p. 172° , yielding a semicarbazone, m. p. 190° , and a phenylhydrazone, m. p. 145° , and on reduction the corresponding secondary alcohol, β -hydroxypropyl *p*-carbamidophenyl ether,



which forms colourless crystals, m. p. 176° , having a faintly sweet after-taste.

G. F. M.

Constitution of Picrorocelin, a Diketopiperazine Derivative from *Rocella fuciformis*. MARTIN ONSLOW FORSTER and WILLIAM BRISTOW SAVILLE (T., 1922, 121, 816-827).

New Syntheses of Pyrimidines. E. CHERBULIEZ and K. N. STAVRITCH (*Helv. Chim. Acta*, 1922, 5, 267—284).—5-Bromo-

6-hydroxypyrimidine-4-carboxylic acid, $\text{NH} \begin{array}{c} \text{CO} \cdot \text{CBr} \\ \text{CH} = \text{N} \end{array} \text{C} \cdot \text{CO}_2\text{H}$, needles, m. p. 206—207°, with evolution of carbon dioxide (copper salt, $[\text{C}_5\text{H}_2\text{O}_3\text{N}_2\text{Br}]_2\text{Cu} \cdot 2\text{H}_2\text{O}$; ethyl ester, $\text{C}_7\text{H}_7\text{O}_3\text{N}_2\text{Br}$, needles, m. p. 155—156°) results from the action of sodium hypobromite on methyleneasparagine. 5-Bromo-6-hydroxypyrimidine, $\text{C}_5\text{H}_3\text{ON}_2\text{Br}$, m. p. 197° (picrate, $\text{C}_{10}\text{H}_8\text{O}_8\text{N}_5\text{Br}$, yellow prisms, m. p. 150—151°; hydrochloride, m. p. 206—207°), obtained by fusion of the carboxylic acid, is converted by the action of phosphoryl chloride into 6-chloro-5-bromopyrimidine, $\text{C}_5\text{H}_3\text{N}_2\text{ClBr}$, b. p. 95.5°/26 mm. (picrate, sparingly soluble in ether), and by reduction with zinc dust into 6-hydroxypyrimidine (Wheeler, A., 1907, i, 879). The last compound also results from the distillation of 6-hydroxypyrimidine-4-carboxylic acid, $\text{C}_5\text{H}_3\text{O}_3\text{N}_2\text{H}_2\text{O}$, prisms, m. p. 268—270° (decomp.), which is itself prepared either by oxidation of methyleneasparagine with alkaline permanganate, or from the above bromo-acid and zinc dust.

Similar series of compounds may be prepared from the alkylidene- and arylidene-asparagines, and the reactions have a special interest in view of the natural occurrence of asparagine and of pyrimidine derivatives.

Ethylideneasparagine, $\text{C}_6\text{H}_{10}\text{O}_3\text{N}_2 \cdot \text{H}_2\text{O}$, needles, m. p. 230—231°, must be prepared by condensation of acetaldehyde with sodium asparaginate. 5-Bromo-6-hydroxy-2-methylpyrimidine-4-carboxylic acid, $\text{C}_6\text{H}_5\text{O}_3\text{N}_2\text{Br}$, prisms, m. p. 209—210° (decomp.), copper salt, $(\text{C}_6\text{H}_5\text{O}_3\text{N}_2\text{Br})_2\text{Cu} \cdot 2\text{H}_2\text{O}$. 5-Bromo-6-hydroxy-2-methylpyrimidine, $\text{C}_5\text{H}_5\text{ON}_2\text{Br}$, prisms, m. p. 231—232° (hydrochloride, m. p. 229—230°; acetate, m. p. 234°; picrate, $\text{C}_{11}\text{H}_8\text{O}_8\text{N}_5\text{Br}$, m. p. 163—164°; silver salt soluble in hot water; copper salt, a green, flocculent precipitate). 6-Chloro-5-bromo-2-methylpyrimidine, $\text{C}_5\text{H}_5\text{N}_2\text{ClBr}$, b. p. 107.5°/27 mm. 6-Hydroxy-2-methylpyrimidine-4-carboxylic acid, $\text{C}_6\text{H}_6\text{O}_3\text{N}_2 \cdot 2\text{H}_2\text{O}$, m. p. 261° (decomp.), basic copper salt, $\text{C}_6\text{H}_5\text{O}_3\text{N}_2 \cdot \text{CuOH}$. 6-Hydroxy-2-methylpyrimidine, $\text{C}_5\text{H}_5\text{ON}_2$. 5-Bromo-6-hydroxy-2-phenylpyrimidine-4-carboxylic acid, $\text{C}_{11}\text{H}_7\text{O}_3\text{N}_2\text{Br}$, needles, m. p. 250—252°. 5-Bromo-6-hydroxy-2-phenylpyrimidine, $\text{C}_{10}\text{H}_7\text{ON}_2\text{Br}$, prisms, m. p. 252°; 6-chloro-5-bromo-2-phenylpyrimidine, $\text{C}_{10}\text{H}_6\text{N}_2\text{ClBr}$, b. p. 193.5°/24 mm., m. p. 130—131°; 2-phenylpyrimidine, $\text{C}_{10}\text{H}_8\text{N}_2$, b. p. 157.5°/25 mm., m. p. 128° (picrate, $\text{C}_{16}\text{H}_{11}\text{O}_8\text{N}_5$, m. p. 108°). 6-Hydroxy-2-phenylpyrimidine-4-carboxylic acid, $\text{C}_{11}\text{H}_7\text{O}_3\text{N}_2$, m. p. 247° (decomp.), copper salt, $(\text{C}_{11}\text{H}_7\text{O}_3\text{N}_2)_2\text{Cu} \cdot 2\text{H}_2\text{O}$, ethyl ester, $\text{C}_{13}\text{H}_{12}\text{O}_3\text{N}_2$, needles, m. p. 84—85°; 5-bromo-6-hydroxy-2-phenylpyrimidine-4-carboxylic acid, $\text{C}_{11}\text{H}_7\text{O}_3\text{N}_2\text{Br}$, m. p. 252°, from the preceding compound and sodium hypobromite, decomposes on fusion into 5-bromo-6-hydroxy-2-phenylpyrimidine; 6-hydroxy-2-phenylpyrimidine (Pinner, A., 1890, 69; Ruhemann and Hemmy, A., 1897, i, 488) yields a picrate, $\text{C}_{16}\text{H}_{11}\text{O}_8\text{N}_5$, yellow needles, m. p. 151°.

J. K.

Preparation of a New Diethylbarbituric Acid Compound. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (Brit. Pat. 158558).—A new compound of diethylbarbituric acid and 4-di-methylamino-1-phenyl-2:3-dimethyl-5-pyrazolone is obtained by melting the two substances together in the proportion of 1 mol. of the former to 2 mols. of the latter, and purifying the product in the usual manner. The new compound is yellow in colour, melts at 95–97°, and has strong analgesic properties, whilst the hypnotic effect is repressed.
G. F. M.

The Nature of Isatoids. GUSTAV HELLER and WALTER BENADE (*Ber.*, 1922, 55, [B], 1006–1014; cf. Heller, A., 1920, i, 766; 1921, i, 891; Hantzsch, A., 1921, i, 597).—The existence of the alkylisatoids of von Baeyer and Oekonomides has been confirmed by Heller but denied by Hantzsch; their preparation and behaviour has again been examined in detail.

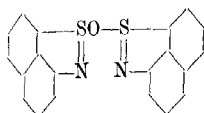
Methylisatoid is obtained when isatin silver is subjected to the action of methyl iodide in the presence of benzene at 100° and the filtrate, after removal of re-formed isatin and silver iodide, is allowed to evaporate spontaneously while exposed to light. The residue is recrystallised from glacial acetic acid and yields thereby β -methylisatoid. The latter passes into the α -form when recrystallised rapidly from benzene, but appears to undergo further change on protracted heating with this solvent. The α - is converted into the β -variety by recrystallisation from glacial acetic acid. Ethylisatoid, prepared in a similar manner, forms red rhombohedra, m. p. 218–219° (decomp.) after darkening at 211–212°. Contrary to the statement of Hantzsch, the melting points of the methyl and ethyl compounds are quite distinct from one another. Curiously, a mixture of equal amounts of the two substances has a slightly higher melting point. *n*-Propyl iodide and isatin silver give *n*-propylisatoid, quadratic prisms, m. p. 187° (decomp.) after darkening at 180°; attempts to convert it into a desmotropic form resulted in the production of a yellow, flocculent precipitate, m. p. about 177° (decomp.). *iso*Butyl iodide and isatin silver yield a substance, m. p. 147–148°, which by reason of the small amount available could not be further investigated.

The alkyl group of the alkylisatoids can be removed by treatment with glacial acetic acid and hydrogen bromide, but, unexpectedly, the substance obtained after addition of sodium acetate to the solution is found to be anhydroindoxyl- α -anthranilide, $\text{CO}-\text{CH}\cdot\text{NH}$
 $\text{C}_6\text{H}_4\cdot\text{N}-\text{CO}$ C_6H_4 , brownish-red plates, m. p. 217–218° (decomp.); the mechanism of the addition of the two atoms of hydrogen during the hydrolysis has not been established. The substance is smoothly oxidised by chromic acid to anhydro- α -isatinanthranilide (Friedländer and Roschdestwensky, A., 1916, i, 80). It thus appears to be established that the union of the isatin molecules in the isatoids is accomplished by means of the indole nuclei.
H. W.

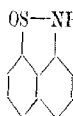
Benzbisthiazoles. STEPHEN RATHBONE HOLDEN EDGE (T., 1922, 121, 772—775).

A New Class of Vat Dyes containing Sulphur and Nitrogen.

ARNOLD REISSERT (Ber., 1922, 55, [B], 858—873).—Erdmann and Süvern have observed that a clear, pale yellow solution is obtained when a salt of 8-nitronaphthalene-1-sulphinic acid dissolved in water is boiled with zinc dust and potassium sulphite; the liquid becomes colourless when acidified with dilute hydrochloric acid and subsequently deposits a blue dye when heated. The latter has now been isolated in the homogeneous condition; it has the empirical formula, $C_{20}H_{12}ON_2S_2$, and the annexed constitution is suggested for it, without, however, being established definitely. It is designated "naphthathiam-blue."



The nitration of naphthalene- α -sulphonyl chloride is carried out in accordance with the directions of Erdmann and Süvern, but an improved method of separating the 1:8- and 1:5-nitronaphthalenesulphonyl chlorides from one another is described in detail. 8-Nitronaphthalene-1-sulphinic acid forms colourless crystals which become brown when exposed to light, decomp. 110° . 5-Nitronaphthalene-1-sulphinic acid has m. p. 140° , and is considerably more stable than the 1:8-isomeride; the sodium and calcium salts are described. 8-Aminonaphthalene-1-sulphinic acid, small, pale-grey, sandy crystals, m. p. 143° (decomp.), is obtained conveniently by the action of sodium hydroxide and ferrous sulphate on the solution obtained by warming 8-nitronaphthalene-1-sulphonyl chloride with sodium sulphite and sodium hydrogen carbonate (the corresponding benzoyl derivative crystallises in colourless, lustrous needles [$-1H_2O$], m. p. $126-127^\circ$ to a dark liquid). It is readily converted into the blue dye when heated in aqueous solution or in the presence of acids. If, however, the solution is treated with so much hydrochloric acid that it just turns Congo paper blue and is allowed to remain at the atmospheric temperature for a day, the dehydration can be arrested at an intermediate stage with the production of naphthathiam (annexed formula), almost colourless needles, which become



converted into the blue dye at $153-155^\circ$ [the corresponding nitroso-compound forms orange-yellow, glistening crystals, m. p. 180° (decomp.)]. The aqueous solution of naphthathiam or of 8-aminonaphthalene-1-sulphinic acid is transformed by warm hydrochloric acid into naphthathiam-blue, which in appearance and solubility exhibits a very close resemblance to indigotin. It gives dull, violet-blue shades on wool and somewhat purer tones on cotton, but has little affinity for the latter. Attempts to elucidate the constitution of the dye by oxidative degradation with nitric or chromic acid were unsuccessful, since only dark-coloured, amorphous products were obtained.

The preparation of derivatives of the dye has also been inves-

tigated in the hope of obtaining further confirmation of its structure. Thus, 8-acetylaminonaphthalene-1-sulphonyl chloride is converted by a mixture of concentrated sulphuric and nitric acids (d 1.52) into 4-nitro-1-acetylaminonaphthalene-5-sulphonyl chloride which, on account of its instability, was not isolated in the pure condition; the crude chloride is converted by sodium sulphite into 4-nitro-1-acetylaminonaphthalene-5-sulphinic acid, pale yellow, microscopic crystals (+H₂O), decomp. 130°, which is transformed in the manner described for the parent dye into *diaminonaphthathiam-blue*, C₂₀H₁₀ON₂S₂(NH₂)₂. A similar series of reactions when applied to naphthionic acid yielded only a trace of dye.

It is shown in the following manner that the presence of the oxygen atom in the dye is not essential to the development of tinctorial properties. 8-Aminonaphthalene-1-sulphinic acid is reduced by stannous chloride and hydrochloric acid to 8-thiol-

α -naphthylamine, which is converted readily by atmospheric oxygen into 1:1'-diaminodinaaphthyl 8:8'-disulphide, small, yellow needles, m. p. 118°; either of these compounds is readily oxidised by air in alcoholic alkaline solution to a blue dye which very closely resembles naphthathiam-blue; it appears to have the composition C₂₀H₁₂N₂S₂, but could not be purified satisfactorily. 8-Thiol- α -naphthylamine yields a *dibenzoyl* derivative, colourless needles, m. p. 202°, which is transformed by boiling alcoholic sodium hydroxide solution into 2-phenylperithiazine (annexed formula), golden-yellow needles, m. p. 102–103°.

Initial difficulties encountered in preparing the amino-mercaptan by the method outlined above have led the author to reduce 8-nitronaphthalene-1-sulphinic acid with hydrogen bromide and glacial acetic acid (cf. Fries and Schürmann, A., 1914, i, 676) to 8:8'-dinitrodinaaphthyl 1:1'-disulphide, m. p. 214°; the sparing solubility of this compound renders the reduction of the nitro-groups in an acid medium very difficult. Attempts to convert it into the nitrothiol by means of alkali and dextrose led unexpectedly to naphthsultam, C₁₀H₆ $\begin{smallmatrix} \text{NH} \\ \text{SO}_2 \end{smallmatrix}$, in consequence of a remarkable migration of the oxygen atoms from nitrogen to sulphur.

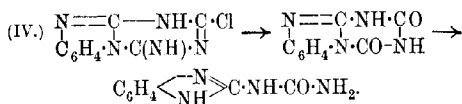
The following compounds have been incidentally prepared: 5-acetylaminonaphthalene-1-sulphinic acid, colourless crystals, incipient decomp. 145°; 4:4'-dinitro-1:1'-diacetylaminodinaaphthyl 5:5'-disulphide, decomp. above 300°; 5-chloronaphthalene-1-sulphinic acid, colourless leaflets, incipient decomp. 220°; 5:5'-dichlorodinaaphthyl 1:1'-disulphide, pale yellow crystals, m. p. 169–170°.

H. W.

The Quindolines. E. GRANDMOUGIN (*Compt. rend.*, 1922, 174, 1175–1177).—Indigotindianilide (cf. A., 1909, i, 968; 1910, i, 73), when warmed with mineral acids, undergoes isomerisation, giving a substance which is apparently an anilide of 5-indoquinolone. It cannot be oxidised to an isatin and on energetic hydrolysis it loses aniline, giving a new compound, C₂₂H₁₅ON₃, which gives

When boiled with hydrochloric acid, the latter gives phenylene-melanuric acid, $\text{N}=\text{C}(\text{OH})\text{—N}(\text{OH})\text{—C}_6\text{H}_4\text{—N}(\text{OH})\text{—C}(\text{OH})=\text{N}$, which is also obtained by the action of nitrous acid on phenyleneammeline.

When heated with alkali hydroxide, *o*-phenyleneammetyl chloride loses ammonia and yields the phenyleneguanylcaramide already obtained from β -cyanophenyleneguanidine and hydrochloric acid (A., 1919, i, 134). Since the same product is formed also from phenylenemelanuric acid, the latter evidently represents an intermediate stage in the reaction:



It is probable that another intermediate product is formed at a still earlier stage by replacement of the chlorine atom alone by a hydroxyl group; such a product would be a phenyleneammeline isomeric with that already described, and may possibly result from gentle hydrolysis of *o*-phenyleneammetyl chloride by means of sodium carbonate, this hydrolysis giving a chlorine-free compound which contains the expected proportion of nitrogen but is amorphous and difficult to purify.

The phenyleneguanylcaramide obtained by hydrolysis of β -cyanophenyleneguanidine by means of hydrochloric acid (*loc. cit.*) crystallises from water in anhydrous, lustrous scales which undergo no change in contact with the water; that obtained according to scheme (IV) and formed in an alkaline medium from which it is precipitated by either acetic or carbonic acid, crystallises from water in long, lustrous, anhydrous needles, but the latter become opaque and take up 2 mols. of water if left in contact with the solvent. A hot aqueous solution of the hydrated crystals deposits the long, lustrous crystals on cooling. These two forms, which behave alike in other respects, are regarded as desmotropic forms of the structures $\text{C}_6\text{H}_4\cdot\text{N}(\text{NH})\text{—C}(\text{NH})\text{—CO}\cdot\text{NH}_2$ and $\text{C}_6\text{H}_4\cdot\text{N}(\text{NH})\text{—C}(\text{NH})\text{—C}(\text{OH})\text{—NH}$, the former probably representing the scales obtained in an acid medium and the latter the needles separating in alkaline solution.

o-Phenyleneammetyl chloride, $\text{C}_6\text{H}_5\text{N}_5\text{Cl}$, separates in microscopic crystals, does not melt but turns yellow at about 220° , and possesses slight acidic and basic functions.

o-Phenylenemelanuric acid, $\text{C}_6\text{H}_6\text{O}_2\text{N}_4$, crystallises in small needles and decomposes, without melting, at 300° . This compound also appears to exist in two desmotropic forms. T. H. P.

Catalytic Preparation of Azobenzene and Aniline. C. O. HENKE and O. W. BROWN (*J. Physical Chem.*, 1922, 26, 324—348; cf. this vol., i, 445, 535).—The action of lead and bismuth as

catalysts on the reduction of nitrobenzene by hydrogen has been investigated with catalysts of various origins and at various temperatures. In the presence of lead as catalyst, nitrobenzene is reduced by hydrogen to azoxybenzene, azobenzene, and aniline. It is shown that lead prepared by reducing yellow litharge is the best catalyst for the production of azobenzene, and that the action is best carried out in an iron tube at 290°. The best catalyst for aniline in an iron tube is lead prepared by the reduction of red lead from white lead. In this case, the efficiency is greatest above 308°. A catalyst when used in a glass tube gives a higher yield of azobenzene and a lower yield of aniline than when used in an iron tube, but the activity of the catalyst decreases much more rapidly in glass than in iron. In a glass tube, the catalyst from white lead is best for producing aniline, and the one from red lead made from white lead is best for producing azobenzene. The addition of sodium hydroxide and magnesia to the lead catalyst in an iron tube does not increase its activity and a larger amount of sodium hydroxide decreases it. The addition of 0.5% of ferric oxide to a lead catalyst from a heavy litharge increases the yield of both azobenzene and aniline, whilst 5% of ferric oxide increased the yield of aniline at the expense of the azobenzene. The addition of 5% of cupric oxide to the same catalyst was detrimental to its activity. Within the limits of the present experiments, it is found that the more finely divided the red lead from which the catalyst is prepared the more active the catalyst. The best yield of azobenzene was obtained when lead from yellow litharge was heated in an iron tube at 290° and nitrobenzene passed over at the rate of 4 grams per hour and hydrogen at the rate of 17 litres per hour. In this case the material yield was 55.4% of azobenzene and 26.0% of aniline. Using sublimed litharge to produce the catalyst the yield is 61.1% of aniline and 34.4% of azobenzene at 310°, whilst when lead from white lead is used at 303°, the yield is 74.9% of aniline and 21.0% of azobenzene, all other conditions being the same as stated above.

Nitrobenzene is reduced to azoxybenzene, azobenzene, hydrazobenzene, and aniline by hydrogen with bismuth as catalyst. Using equal volumes of catalyst, that prepared from heavy bismuth oxide is more active than one prepared from the light oxide. The activity of the bismuth does not decrease so rapidly when used in an iron tube as when used in a glass tube. A good temperature to use the bismuth catalyst is between 280° and 300°. When the tube is fed with nitrobenzene at the rate of 4.2 grams per hour and hydrogen at 17 litres per hour the following optimum yields are obtained: with bismuth from the heavy oxide in an iron tube at 230°, a yield of 92% of azobenzene and 4.4% of aniline, whilst under the same conditions at 300° the yield is 73.9% of aniline and 19.3% of azobenzene.

J. F. S.

Facts and Theories in the Constitution of the Hydroxyazo-compounds. E. PUXEDDU and MARCELLA GENNARI (*Gazzetta*, 1922, 52, i, 216—229).—The authors discuss more particularly

the literature dealing with the reduction of the hydroxyazo-compounds and their acyl derivatives, the action of phenyl cyanate on hydroxyazo-compounds, the action of carbon disulphide at a high temperature on *o*-hydroxyazo-compounds, preparation of *m*-hydroxyazobenzene and its significance, isomerisation of the quinonic compounds, and physico-chemical investigations on the hydroxyazo-compounds.

All the results obtained support the view that the hydroxyazo-compounds of the ortho-series are to be differentiated from those of the meta- and para-series. The insolubility of most of the *o*-hydroxyazo-compounds in the calculated proportion or even in considerable excess of alkali hydroxide presents a serious objection to the classification of these compounds as phenolic; that some do dissolve is merely an indication of the instability of the quinonoid structure and of its tendency to become azophenolic.

The behaviour of the acyl derivatives during reduction furnishes a certain proof of the azophenolic constitution of the para- and the hydrazonic constitution of the ortho-compounds, notwithstanding the fact that it has been shown that in an aromatic nucleus acyl groups in the ortho-position to a chain containing aminic or iminic hydrogen may pass from the oxygen to the nitrogen during reduction. Such migration during the reduction of acyl-*o*-hydroxyazo-compounds would demonstrate undoubtedly their azophenolic structure, but no such proof exists, and the behaviour of acetyl-*p*-chlorobenzeneazo-*p*-cresol is an exception to the general rule expressing the difference in behaviour of the ortho-compounds from their meta- and para-isomerides. On the other hand, assumption of azophenolic constitutions for *o*-hydroxyazo-compounds on the basis of migration of the acyl group would necessitate the hypothesis that the acyl exchanges position, not with the hydrogen immediately adjacent to it, but with the second hydrogen of the hydrazo-group.

The proofs advanced of the instability of the quinonoid nuclei in the acyl derivatives of *o*-hydroxyazo-compounds require a greater abundance and more uniformity of experimental results before the latter may be regarded as justifying the azophenolic constitution of these ortho-compounds.

The behaviour towards phenylcarbimide scarcely differentiates clearly between the ortho- and para-compounds since the former react, after some weeks, in the same way as the latter, but it shows that the carbimide exerts a double action on ortho-compounds, first converting them into azophenolic compounds and then combining with these.

The conclusions drawn are that both free hydroxyazo-compounds and their acyl derivatives behave as tautomeric substances; that free *p*- and *m*-hydroxyazo-compounds and their acyl derivatives are always phenolic in type; that *o*-hydroxyazo-compounds, both in the free condition and as acyl derivatives, must be regarded as of quinono-hydrazonic configuration, with a pronounced tendency to pass into the more stable azophenolic form; and that the meso-hydric formula of Oddo and Puxeddu (A., 1906, i, 991; 1907, ii, 15),

giving a representation of the phenomenon of desmotropy, provides a very simple scheme applicable to all analogous phenomena.

T. H. P.

Degree of Hydrolysis of Alkali Salts of Hydroxyazo-compounds. E. PUXEDDU (*Gazzetta*, 1922, 52, i, 235—238; cf. A., 1921, i, 366, 623).—The ordinary methods of determining the degree of hydrolysis are inapplicable to the alkali salts of the hydroxyazo-compounds, since the results are affected by the presence of the sparingly soluble free hydroxyazo-compound, which separates as the hydrolysis proceeds.

The author has carried out conductivity measurements on alkaline solutions of sodium and potassium derivatives of various *p*-hydroxyazo-compounds after different intervals of time, vessels filled with the solutions being kept tightly closed in the dark at constant temperature. It is found that the conductivity of such a solution varies markedly with the time, the equilibrium $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{ONa} + \text{H}_2\text{O} \rightleftharpoons \text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH} + \text{NaOH}$ undergoing displacement owing to the separation of increasing proportions of the free hydroxyazo-compound.

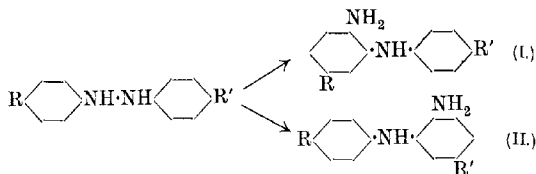
The degree of hydrolysis may, however, be determined by extracting the hydrolysed compound by means of ether. The hydroxyazo-compound is dissolved in the required quantity of sodium hydroxide solution of known titre and the solution made up to a definite dilution and immediately shaken energetically for a few seconds with ether; the ethereal layer is separated, washed and dried with sodium sulphate, and evaporated in a platinum dish, the residue being weighed. This method gives concordant results, provided that the extraction with ether is carried out with the necessary rapidity; it is applicable also when the product of the hydrolysis remains completely dissolved in the aqueous solution, provided that the alkali salt is insoluble, and the above product readily soluble, in ether. The sodium derivatives of benzeneazo-*p*-phenol, *o*-tolueneazophenol, and benzeneazo-*o*-cresol have been examined in this way.

T. H. P.

The Isomeric Changes of Hydrazo-compounds. PAUL JACOBSEN (*Annalen*, 1922, 427, 142—221).—The paper is in four parts.

(A) *Isomeric Changes of Doubly Para-substituted Hydrazo-compounds* [with D. R. BOYD, M. FREUND, H. L. FULDA, F. HEUBACH, H. JOST, G. LOCKEMANN, A. LOEB, J. PEIZER, W. SACHS, H. TIGGES, and K. ZAAR].—Hydrazo-compounds of this class cannot pass into *p*-semidines without loss of one of the para-substituents, but they are capable of yielding *o*-semidines if the necessary ortho-positions are free. In seven out of the eight cases investigated an *o*-semidine was isolated and identified; in the eighth it was detected by qualitative reactions.

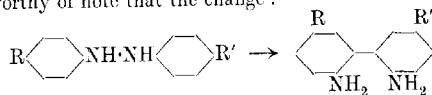
When the groups in the two para-positions are different, the formation of an *o*-semidine can take place in two ways:



so that the relative directing powers of the groups R and R' can be determined. If the semidine I were the main product, the conclusion would be that the group R had a greater directing power than R'. It is remarkable that in none of the cases examined was more than one *o*-semidine isolated, but this does not by any means prove that these conversions take place only in one direction, because a secondary product would be quite likely to escape detection. The groups R and R' were of the following: Br, I, OEt, OAc, NMe₂, Me. An examination of the data shows that of all these the ethoxyl group has the strongest directing power, the methyl group being next in order.

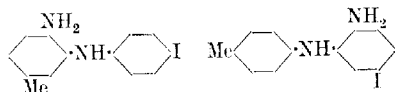
Hydrazo-compounds in which one of the para-substituents was an acetoxy group gave *p*-semidines, the acetoxy group being eliminated.

It is worthy of note that the change :



was not realised, and it is to be presumed that there is a strong resistance to the formation of this grouping by the isomeric change of hydrazo-compounds of the benzene series (see below).

(i) *Isomerisation of 4'-Iodo-4-methylhydrazobenzene.*—The *o*-semidine obtained from this substance has the first of the following formulæ :



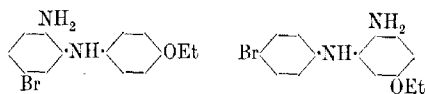
The isomeric substance was synthesised by condensing 4-iodo-1:2-dinitrobenzene with *p*-toluidine and reducing the product.

4'-Iodo-4-methylazobenzene is obtained as golden-red leaflets, m. p. 165–166°, when 4'-amino-4-methylazobenzene is diazotised and treated with potassium iodide. On reduction by means of ammonium sulphide it gives 4'-iodo-4-methylhydrazobenzene, colourless needles, m. p. 134°, whilst with alcoholic stannous chloride it yields, besides *p*-iodoaniline and *p*-toluidine, 4'-iodo-2-amino-5-methyldiphenylamine, m. p. 116–117°, which gives the usual reactions of an *o*-semidine with nitrous acid, with benzil (the stilbazonium base forms yellowish-green, microscopic needles, m. p. 166–168°), with salicylaldehyde (the *anhydro*-derivative

forms yellow needles, m. p. 132—134°) and with carbon disulphide. The product of the last reaction, 2-mercapto-1-*p*-iodophenyl-6-methylbenziminazole, forms fine, colourless needles, m. p. 284—285°, yields a mercury salt on treatment with mercuric oxide, and a *S*-methyl ether, m. p. 139—140°, with methyl iodide. 5-Iodo-2-nitro-4'-methyl-diphenylamine forms red needles, m. p. 104°. 5-Iodo-2-amino-4'-methyl-diphenylamine, forms colourless leaflets, m. p. 86—87°; its anhydro-base with salicylaldehyde forms yellow needles, m. p. 148°.

(ii) *Isomerisation of 4'-Ethoxy-4-methylhydrazobenzene*.—The conversion of this substance into an *o*-semidine has previously been described (A., 1896, i, 24). The semidine is now further characterised by its anhydro-base with salicylaldehyde, m. p. 121—124°, and its constitution proved by synthesis from the condensation product of *p*-toluidine with 4-chloro-1:2-dinitrobenzene. This substance on treatment with sodium ethoxide yields 2-nitro-5-ethoxy-4'-methyl-diphenylamine, bright brown needles, m. p. 104°; this, on reduction by means of ammonium sulphide at 130°, gives 2-amino-5-ethoxy-4-methyl-diphenylamine, identical with the substance obtained from the hydrazobenzene.

(iii) *Isomerisation of 4-Bromo-4'-ethoxyhydrazobenzene*.—This substance could yield the following semidines:

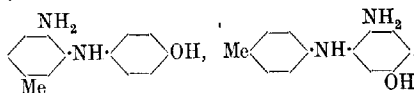


The substance actually isolated was different from the first of these compounds, which was synthesised from 4-bromo-1:2-dinitrobenzene and *p*-phenetidine in the manner previously illustrated.

4-Bromo-4'-ethoxyazobenzene, yellow leaflets, m. p. 135—136°, is formed by ethylating *p*-bromobenzenecazophenol. 4-Bromo-4'-ethoxyhydrazobenzene, which is obtained in good yield by reduction of the azo-compound with zinc dust and alcoholic sodium hydroxide, crystallises in small, colourless needles, m. p. 81—83°. 4'-Bromo-2-amino-5-ethoxydiphenylamine (the semidine obtained from the hydrazo-compound) forms colourless needles, m. p. 67—68°; it gives the nitrous acid reaction and forms a stilbazonium base ($C_{14}H_{15}ON_2Br$) with benzil. On treatment with amyl nitrite, it gives 1-*p*-bromophenyl-6-ethoxybenzotriazole, leaflets, m. p. 145—146°, and with formic acid, 1-*p*-bromophenyl-6-ethoxybenziminazole, needles, m. p. 120°, which on hydrolysis with acids yields 1-*p*-bromophenyl-6-hydroxybenziminazole, pale violet needles, m. p. 295°. With carbon disulphide, the semidine yields 1-*p*-bromophenyl-2-mercapto-6-ethoxybenziminazole, needles, m. p. 253°, and with salicylaldehyde an anhydro-base ($C_{21}H_{19}O_2N_2Br$), m. p. 151°. 5-Bromo-2-nitro-4'-ethoxydiphenylamine, obtained by condensing 4-bromo-1:2-dinitrobenzene with *p*-phenetidine, forms deep red needles, m. p. 115°. The reduction product, 5-bromo-2-amino-4'-ethoxydiphenylamine, is difficult to obtain in a crystalline condition,

but is characterised by the formation of 6-bromo-1-*p*-ethoxyphenylbenzotriazole, m. p. 129°, and by the salicylidene derivative, m. p. 146—147°.

(iv) *Isomerisation of 4'-Acetoxy-4-methylhydrazobenzene*.—The isomeric change of this substance was investigated by reducing the corresponding azo-compound with an acid reagent. Elimination of the acetyl group occurred during the formation of the *o*-semidine, which must have one of the following formulæ :

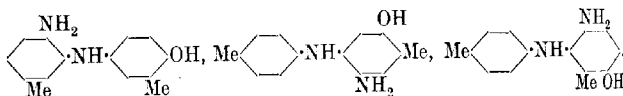


On converting the *o*-semidine into the triazole and then ethylating the hydroxyl group, a product is obtained which is isomeric with the triazole derived from the semidine described in section (ii). If the second of the above formulæ were correct, the substances should be identical. The first formula is thus indicated and its correctness is confirmed by the fission of the substance to quinol and 3:4-tolylenediamine.

Along with the *o*-semidine a *p*-semidine, 4'-amino-4-methyldiphenylamine, is produced with the elimination of the acetoxy group.

2-Amino-4'-hydroxy-5-methyldiphenylamine forms colourless needles, m. p. 137°, but turns red in contact with air. The stillbazonium base was not obtained in a pure condition. The triazole (1-*p*-hydroxyphenyl-6-methylbenzotriazole), however, forms yellow leaflets, m. p. 187.5—189.5°, and on ethylation with ethyl iodide and sodium ethoxide gives 1-*p*-ethoxyphenyl-6-methylbenzotriazole, m. p. 91°.

(v) *Isomerisation of 4'-Acetoxy-3':4-dimethylhydrazobenzene*. This *o*-semidine conversion also is accompanied by the elimination of the acetyl group. The product may have any of the following formulæ :



The third of these is improbable on general grounds, and the second can be proved to be incorrect by ethylating the hydroxyl group of the corresponding iminazole. If the second formula were correct, the product should be the iminazole corresponding with a known semidine, which it is not. The first formula remains, and it is supported by the analogy with the lower homologue (section iv).

In this case also a *p*-semidine is formed with elimination of the acetoxy group.

4'-Acetoxy-3':4-dimethylazobenzene is prepared by heating *p*-tolueneazo-*o*-cresol with sodium acetate and acetic anhydride. It forms thick leaflets or nodular aggregates of fine needles, m. p. 65—66°. On reduction under the usual conditions it is converted

into fission products and the semidines. 2-Amino-4'-hydroxy-3':5'-dimethyldiphenylamine is difficult to purify, but on heating with formic acid it gives 1:6-hydroxy-m-tolyl-6-methylbenzimidazole, glistening leaflets, m. p. 196—197° (nitrate sparingly soluble, hydrochloride forms white leaflets). On ethylation, this substance gives 1:6-ethoxy-m-tolyl-6-methylbenzimidazole, which forms a well-defined hydrochloride (needles) and a picrate (prisms, m. p. 186—187°). The isomeric compound, 6-ethoxy-5-methyl-1-p-tolylbenzimidazole, prepared from 2-amino-5-ethoxy-4:4'-dimethyldiphenylamine, crystallises with extraordinary ease in fine needles, m. p. 102.5°. Its hydrochloride and nitrate are difficultly soluble and the picrate forms needles, m. p. 228°. 4-Amino-2:4'-dimethyldiphenylamine forms glistening needles, m. p. 78.5°, and behaves as a *p*-semidine towards ferric chloride and nitrous acid. The salicylaldehyde derivative, $C_6H_4Me \cdot NH \cdot C_6H_3Me \cdot N : CH \cdot C_6H_4 \cdot OH$, forms needles, m. p. 116.5°.

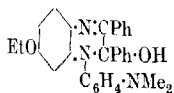
(vi) *Isomerisation of 4-Bromo-4'-acetoxyhydrazobenzene*.—The main product of this isomeric change (which was examined by reducing the azo-compound) is the *p*-semidine, the formation of which involves the extrusion of the acetoxy group. An *o*-semidine was not isolated, but its presence was proved by the formation of a stilbazonium base.

4-Bromo-4'-aminodiphenylamine (the *p*-semidine) forms colourless needles, m. p. 93.5°, and gives a sparingly soluble hydrochloride and sulphate. It gives colorations with nitrous acid and ferric chloride, and on oxidation by means of chromic acid yields quinone. Its salicylidene derivative, $C_6H_4Br \cdot NH \cdot C_6H_4 \cdot N : CH \cdot C_6H_4 \cdot OH$, forms yellow leaflets, m. p. 172°.

(vii) *Isomerisation of 4'-Dimethylamino-4-methylhydrazobenzene*.—The chief product is the *o*-semidine formed under the directive influence of the methyl group (cf. Boyd, T., 1894, 65, 879).

(viii) *Isomerisation of 4'-Dimethylamino-4-ethoxyhydrazobenzene*.—The structure of the *o*-semidine produced by the isomeric change of this hydrazo-compound was proved by synthesis. The product of condensation of *as*-dimethyl-*p*-phenylenediamine with 4-chloro-1:2-dinitrobenzene was ethoxylated and the ethoxy-compound reduced.

4'-Dimethylamino-4-ethoxyazobenzene is obtained in good yield by coupling diazotised *p*-phenetidine with dimethylaniline. It forms brown, oblique, four-sided tablets, m. p. 149—150°. 2-Amino-4'-dimethylamino-5-ethoxydiphenylamine is produced along with the usual fission products when the azo-compound is reduced with stannous chloride. It cannot be crystallised, and must be characterised by derivatives. 1-*p*-Dimethylaminophenyl-6-ethoxybenzimidazole, obtained with the aid of formic acid, forms small needles, m. p. 141—143°. The stilbazonium base, annexed formula, prepared by condensation with benzil, forms canary-yellow needles, m. p. 187—190°. The salicylaldehyde derivative, $C_{23}H_{25}O_5N_3$, forms golden-yellow leaflets having a green metallic reflex, m. p. 141.5—142.5°.



and 6-ethoxy-1-*p*-dimethylaminophenyl-2-*o*-hydroxyphenyl-6-benzimidazole, the condensation product with salicylic acid, forms white, glistening needles, m. p. 182—183°. 5-Chloro-2-nitro-4'-dimethylaminodiphenylamine is prepared from *as*-dimethyl-*p*-phenylene-diamine and 4-chloro-1:2-dinitrobenzene. It forms small, reddish-brown needles, m. p. 181°, and with sodium ethoxide gives 2-nitro-4'-dimethylamino-5-ethoxydiphenylamine, small, deep brown crystals, m. p. 122—123°, which on reduction gives the above semidine.

(ix) Semidines are not obtained on reduction of 4-amino-4'-dimethylaminoazobenzene, 4-acetyl-amino-4'-dimethylaminoazobenzene, or 4:4'-bis-dimethylaminoazobenzene.

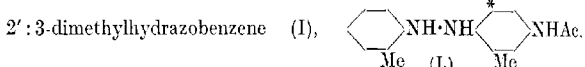
(x) The observations of Meisenheimer and Witte (A., 1904, i, 193) on the conversion of $\beta\beta'$ -azonaphthalene into 2:2'-diamino-1:1'-dinaphthyl are confirmed. This reaction has very few analogies in the benzene series (cf., however, Boyd, Diss., Heidelberg, 1896).

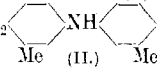
2:2'-Bis-*p*-methoxybenzylideneamino-1:1'-dinaphthyl, prepared from 2:2'-diamino-1:1'-dinaphthyl and anisaldehyde, is a yellow, crystalline powder, m. p. 194—195°.

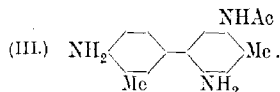
(B) *Isomeric Changes of Singly Para-substituted Hydrazo-compounds* [with M. JAENICKE and G. LOCKEMANN]; cf. A., 1909, i, 852].—

(i) The extension of a meta-substituent during semidine formation has not previously been observed. 4-Methoxyazobenzene-3-carboxylic acid on reduction by means of tin and hydrochloric acid yields 2-amino-5-methoxydiphenylamine together with fission products.

(ii) A remarkable instance of the directive effect of a group in the meta-position is provided by the isomerisation of 4-acetyl-amino-

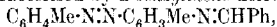


The yield of *p*-semidine (II), , is very small, the main product being a diphenyl base (III),



The isomerisation of *p*-acetylaminohydrazobenzene gives rise only to the *p*-semidine, and the formation of the diphenyl base from the dimethyl homologue must be considered as due to para-direction (that is, to the position marked *) from the methyl group.

4-Amino-2':3-dimethylazobenzene, the acetyl derivative of which on reduction by means of stannous chloride gives the products mentioned, is characterised by a *benzylidene* derivative,

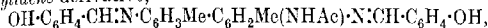


deep red prisms, m. p. 96—97°, and a *salicylidene* derivative, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, orange-yellow needles or

leaflets, m. p. 111—112°. 4-Amino-4'-acetyl-amino-3:3'-dimethyl-diphenylamine forms small, white crystals, m. p. 174—175°, and gives a *salicylidene* derivative,

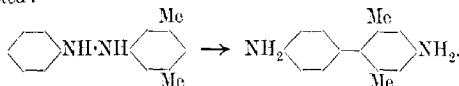


which crystallises in small, yellow needles, m. p. 185—186°. 2:4'-Diamino-5-acetyl-amino-3':4'-dimethyldiphenyl is difficult to purify, but it forms a crystalline *dibenzylidene* derivative, $\text{CHPh}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{C}_6\text{H}_3\text{Me}(\text{NHAc})\cdot\text{N}\cdot\text{CHPh}$, m. p. 204—205°, a *salicylidene* derivative,



m. p. 239—240°, and an acetyl derivative, 2:4':5-triacetyl-triamino-3':4'-dimethyldiphenyl, m. p. 360°.

(C) *The Isomerisation of Hydrazo-compounds which are not Para-substituted* [with F. HÖNIGSBERGER and L. HUBER].—The example studied was 3:5-dimethylhydrazobenzene. A *p*-semidine was not isolated, but the product contained a large amount of a diphenyl base, which, from the fact that it yielded 2:6-dimethyldiphenyl on elimination of the amino-groups, must have the structure indicated:



3:5-Dimethylazobenzene is prepared by condensing nitrosobenzene with *m*-xylydine. It is a deep red oil, b. p. 197.5°/17—19 mm., d_{20}^{20} 1.060. On reduction by means of zinc dust and alkali, it gives 3:5-dimethylhydrazobenzene, which crystallises in long, slender, colourless needles, m. p. 78—79°. 4:4'-Diamino-2:6-dimethyldiphenyl, the main product of isomerisation, forms colourless needles, m. p. 124°, and gives a benzaldehyde derivative, 4:4'-dibenzylidenediamino-2:6-dimethyldiphenyl, which forms pale yellow, hair-like needles, m. p. 199—200°. On eliminating the amino-groups by reducing the diazonium salt with hypophosphorous acid, 2:6-dimethyldiphenyl is obtained, which boils at 260—265°, and is characterised by a *trinitro*-derivative, m. p. 257—258°, and a *tetranitro*-derivative, m. p. 227—229°. The same hydrocarbon was prepared from *v-m*-xylydine (2-amino-1:3-xylene) by treating its dry hydrochloride with ethyl alcoholic amyl nitrite and allowing the diazonium chloride so produced to react with benzene in the presence of aluminium chloride. The isomeric hydrocarbon, 2:4-dimethyldiphenyl, prepared in a similar way from *as-m*-xylydine is an oil, b. p. 270—276°, and forms a *tetranitro*-derivative, m. p. 154.5—155°.

(D) *An Attempt to Generalise the Isomeric Change of Hydrazo-compounds* [with H. JOST, ST. PINKUS, and P. SCHMIDT].—Three types of hydrazo-compounds (or the desmotropic hydrazones) have been examined. (a) Compounds, $\text{R}\cdot\text{NH}\cdot\text{NH}\cdot\text{R}'$, in which R is aromatic and R' purely aliphatic, (b) compounds in which R is aromatic and R' is a residue such as benzyl in which an aromatic nucleus is joined indirectly to the hydrazo-group, (c) compounds

in which both R and R' are residues of this kind. Changes analogous to the semidine and benzidine conversions have not been observed in these cases.

Pyruvaldehyde p-ethoxyphenylhydrazone,
 $\text{COMe}\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$,

orange-yellow leaflets, m. p. $144\cdot5^\circ$, is formed by condensing acetoacetic acid with diazotised *p*-phenetidine; *di-p-ethoxyphenylformazyl methyl ketone*, $\text{COMe}\cdot\text{C}(\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, small, deep red needles, m. p. 143° , is also formed. *Pyruvic acid p-ethoxyphenylhydrazone*, canary-yellow needles, m. p. $120\text{--}122^\circ$, is obtained by condensing ethyl methylacetoacetate with diazotised *p*-phenetidine and hydrolysing the product (m. p. 110°). On reduction by means of sodium amalgam, it yields α -*p-ethoxyphenylhydrazinopropionic acid*, pale yellow needles, m. p. $128\text{--}138^\circ$.

C. K. I.

Summary of Results on the Isomeric Changes of Hydrazo-compounds, and Considerations relating to the Possibilities of their Explanation. PAUL JACOBSEN (*Annalen*, 1922, 428, 76—121).—An ordered summary of all previous work on the subject of this isomeric change, and a discussion of the principal views which have been expressed.

C. K. I.

The Action of Amines on Semicarbazones. I. Preparation of an Optically Active Semicarbazide. FORSYTH JAMES WILSON, ISAAC VANCE HOPPER, and ARCHIBALD BARCLAY CRAWFORD (T., 1922, 121, 866—870).

Reactions of Thiosemicarbazones. I. Action of Halogen Compounds. FORSYTH JAMES WILSON and ROBERT BURNS (T., 1922, 121, 870—876).

Is the Heat-coagulation of Protein a Hydrolysis? MARGIT HIRSCH-POGANY (*Biochem. Z.*, 1922, 128, 396—401).—The author has attempted to determine whether the heat-coagulation of egg-white is due to hydrolysis by determining the increase in weight and the increased content of hydrogen and oxygen by analysis. The changes found were too small to indicate hydrolysis with any certainty.

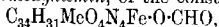
H. K.

Fibrinolysis. II. MAX ROSENMANN (*Biochem. Z.*, 1922, 128, 372—381).—The fibrinolytic agent for which the authors adopt the name *thrombolsin* is precipitable by alcohol, ammonium sulphate, and zinc chloride. It exhibits maximum activity at 37° and in neutral solution. It is inactivated at $46\text{--}48^\circ$. Fibrin heated at $57\text{--}62^\circ$ is no longer acted on by thrombolsin. The best solution for preserving the active material is 25% alcohol. Human and horse fibrin behave similarly towards thrombolsin.

H. K.

The Prosthetic Group of Blood Pigment. Formoxy-hæmin. WILLIAM KÜSTER and ADOLF GERLACH (*Z. physiol. Chem.*, 1922, 119, 98—116).—The hæmatin-like substance obtained by Partos (A., 1920, i, 773) by the action of methyl alcohol con-

taining formic acid on blood-coagulum is found to be an inner salt of *monomethylformoxyhæmin*, of the constitution



fine, slender needles, insoluble in water and all organic solvents, including aniline and pyridine, and in 5% sodium carbonate solution at the ordinary temperature, whilst it dissolves slowly in 5% sodium carbonate solution on heating, and in cold 1% sodium hydroxide solution. On digestion with methyl alcohol containing sulphuric acid, it slowly dissolves, and from the solution by the addition of hydrogen chloride, a β -*dimethylchlorohæmin*, $\text{C}_{36}\text{H}_{36}\text{O}_4\text{N}_4\text{FeCl}$, small deformed needles, can be isolated.

Attempts to prepare α - and β -formoxyhæmins have not resulted in obtaining chlorine-free compounds.

Acetyloxyhæmin, a microcrystalline black powder, of the formula $\text{C}_{36}\text{H}_{35}\text{O}_6\text{N}_4\text{Fe}$, is obtained by the action of ethyl alcohol and acetic acid on oxyhæmoglobin powder.

W. O. K.

The Hæmochrome of Herzfeld and Klinger. S. PARTOS (*Biochem. Z.*, 1922, 129, 89—100).—An extensive comparison of Herzfeld and Klinger's hæmochrome (A., 1920, i, 731) and hæmatin establishes their identity.

H. K.

Physical Characteristics of Gelatin Solutions. CLARKE E. DAVIS and EARLE T. OAKES (*J. Amer. Chem. Soc.*, 1922, 44, 464—479; cf. this vol., i, 63).—In the present paper, the variation of the density of gelatin solutions with temperature between 0° and 60°, the variation of density with concentration at 40°, the transition point of gel to sol, the variation of viscosity with concentration at 40°, the variation of viscosity with temperature from 25° to 60°, and the variation of viscosity with the hydrogen-ion concentration at 40° have been determined. It is shown that the density of a gelatin solution, expressed in grams per c.c., at any temperature and any concentration, is equal to the density of water at that temperature plus 0.00290 multiplied by the percentage concentration of the gelatin by weight. The viscosities of gelatin solutions of various concentrations at 40° conform with Arrhenius's viscosity formula. The viscosity-temperature curve of gelatin solutions shows a sharp deflexion at the transition point of gelatin. There are two maxima in the viscosity-hydrogen-ion concentration curve for gelatin solutions at 40°. These maxima are equidistant from the neutral point of water, and the effect of the isoelectric point, $P_H=4.7$, is not noticeable on the curve. The transition point of gelatin sol form A \rightleftharpoons gel form B is a temperature of 38.03°.

J. F. S.

Protein Enzymes. RUDOLF EHRENBERG (*Biochem. Z.*, 1922, 128, 431—449).—The author revives a hypothesis of enzyme action similar to that of Liebig. The enzyme is not a resting definable entity, but is a process into which the substrate may be induced to pass under certain conditions. The hypothesis is illustrated at length by reference to experiments on trypsin and pepsin.

H. K.

Rôle of Acids in Peptic Digestion. Wo. OSTWALD and A. KUHN (*Kolloid Z.*, 1922, **30**, 234—243).—The swelling of gelatin and egg-albumin by solutions of sulphosalicylic acid has been investigated at various temperatures between 13.7° and 20.2°. It is shown that sulphosalicylic acid brings about the swelling of gelatin in exactly the same way as other acids, that is, it accelerates it in small concentrations, but retards it when present in greater concentrations. In the case of egg-albumin the sol swelling is furthered by small concentrations of sulphosalicylic acid and a precipitation is brought about by larger concentrations. In earlier papers, it has been shown that the swelling of the substrate plays an important part in peptic digestion, inasmuch as a furtherance of the swelling by acids also brings about a furtherance of the fermentation process. In opposition to this rule, Gyemant (A., 1920, i, 783), and Michaelis (A., 1921, i, 74) have shown that the sulphosalicylic acid which precipitates albumin makes peptic digestion possible. The present work shows that this case does not present an exception to the above-mentioned rule, for sulphosalicylic acid exerts a swelling action in concentrations of the same order as those at which Michaelis and Gyemant found the maximum peptic digestion. J. F. S.

Invertase. II. RICHARD WILLSTÄTTER and FRITZ RACKE (*Annalen*, 1922, **427**, 111—141; cf. A., 1921, i, 823).—An investigation of the nature of the enzymatic process by means of which invertase may be set free from the yeast-cell, and of the condition in which invertase occurs in the cell. The general conclusion is that the invertase occurs as such, and not as a complicated carbohydrate molecule or higher polyose, but that it is protected and prevented from diffusing by the membranes of the cell-structure. The function of the liberating enzymes is to destroy these membranes so that the invertase can diffuse away.

The liberating enzyme is somewhat unstable, and the process which results in the dissolution of the invertase is dependent therefore on the manner in which the yeast is killed. If it is killed, for instance, by water at 50°, by 2% acetic acid, by 50% alcohol, or by cold ethyl acetate, the invertase content is quite unaffected, but its dissolution is hindered owing to the destruction of the liberating enzyme. Invertase itself is not appreciably decomposed by water below 55°.

The following experiment shows the liberating enzyme to be a polysaccharase rather than a proteolytic enzyme. If the yeast is killed by means of warm ethyl acetate (which destroys the enzyme), and either pepsin or trypsin is added, a large part of the yeast (the proteins) passes into solution, but the whole of the original invertase remains in the insoluble portion. If now this is treated with a polysaccharase such as tannase or malt-diaxase, the whole of the invertase is liberated.

There are four ways in which invertase might be supposed to occur in the yeast-cell: (a) as a complex carbohydrate molecule, (b) as a polyose, (c) as adsorbed invertase, (d) as invertase con-

served between the membranes of the cell. If, however, the yeast is ground with an abrasive material for a long period at a temperature too low for any enzymatic process to occur, the whole of the invertase becomes soluble. Moreover, the substance present in this solution evidently does not belong to a more complex molecular species than the invertase obtained by enzymatic action, as can readily be shown by examining its behaviour with various adsorbents. Evidently, therefore, the invertase must exist as such enclosed in protecting membranes, which must be broken before it can diffuse. The destruction of the membranes can be effected by mechanically reducing the cell, but the same result is obtained much more quickly by allowing a polysaccharase to attack the membranes.

The solutions of invertase obtained by subjecting yeast killed by means of warm ethyl acetate, first to proteolysis, and then to diastatic decomposition (fractional enzymatic extraction), are considerably richer than those formed by the action of the enzyme present in the yeast (autolysis). The invertase obtained by either process may be purified by adsorption and isolated as described in the previous paper (*loc. cit.*). The preparations of invertase obtained by fractional enzymatic extraction are comparable in strength with those obtained from solutions formed by autolysis, but whilst the latter are free from carbohydrates and contain proteins, the former are free from proteins and contain carbohydrates. Other impurities which may be present are (a) foreign matter, including mineral substances derived from the adsorbents, (b) decomposed invertase, (c) and other carbohydrate-hydrolysing enzymes, such as raffinase and stachyase.

C. K. I.

The Temperature Coefficients in the Degradation of Starch and the Thermostability of Malt Diastase and Ptyalin. EFR. ERNSTRÖM (*Z. physiol. Chem.*, 1922, **119**, 190—263).—The optimal zone of reaction for malt diastase is P_H 4—6, that of ptyalin is P_H 6·5. Malt diastase is not influenced by the presence of sodium chloride in low concentrations; higher concentrations, however, have an inhibiting action. Ptyalin is inactive in the absence of sodium chloride. Ptyalin and malt diastase retain their activity at 0° . The temperature coefficient of these two enzymes falls with the rising temperature. The constant A of Arrhenius's formula for various ranges of temperature and under various conditions was worked out. The highest stability of malt diastase lies at P_H 5·9, that of ptyalin at P_H 6·0—6·1. The presence of sodium chloride (optimum concentration N 10) greatly enhances the stability of ptyalin; the stability of malt diastase is not affected by the presence of sodium chloride. The inactivation temperature of ptyalin under optimal conditions is $57\cdot5^\circ$, in the absence of sodium chloride it is $51\cdot5$ — 52° . Malt diastase is entirely inactivated when heated for one hour at 60° . The rate of inactivation of malt diastase and of ptyalin is not in accordance with that for a unimolecular reaction, but, as in the case of saccharase, it falls off more quickly than is required by the formula

$$k_t = 1/t \log k_a/k_i.$$

The rate of inactivation in low concentrations increases with the decrease in the concentration of the enzyme. The heated enzymes could not be regenerated. S. S. Z.

The Influence of Hydrogen-ion Concentration on the Action of Pancreatic Amylase. J. TEMMINCK GROLL (*Arch. Néerland. physiol.*, 1922, 6, 445—449).—The optimum range of hydrogen-ion concentration for pancreatic amylase extends from $P_{H}4.6$ to $P_{H}6.8$. On either the acid or alkaline side of this range the activity falls off with great rapidity. C. R. H.

α -Emulsin (Oxynitrilase), δ -Emulsin (Oxynitrilase), and Carboligase. L. ROSENTHALER (*Biochem. Z.*, 1922, 128, 606—607).—Polemical against Nordefeldt (this vol., i, 66) and Neuberg and co-workers (*A.*, 1921, i, 480; this vol., i, 305). H. K.

Classification of Carboligase. C. NEUBERG and J. HIRSCH (*Biochem. Z.*, 1922, 128, 608—609).—Polemical against Rosenthaler (preceding abstract). H. K.

Succinodehydrogenase. ERIK P. WIDMARK (*Skand. Arch. Physiol.*, 1921, 41, 200—220; from *Chem. Zentr.*, 1921, iii, 1362—1363; cf. Battelli and Stern, *A.*, 1911, ii, 132, and Thunberg, *A.*, 1918, i, 140).—The enzyme found in the muscles of horses and cattle, called "succinicoxydone" (Battelli and Stern) or "succinodehydrogenase" (Thunberg) changes succinic acid into fumaric acid with elimination of hydrogen. The course of the reaction may be followed by using methylene-blue as hydrogen acceptor, it being thereby changed into the leuco-base. Directions are given for the preparation of the enzyme, from horse or cattle muscle. The time required for the decoloration of a 0.25% solution of methylene-blue was used as a measure of the reaction of the enzyme with succinic acid. With constant concentration of succinate the decolorising power was proportional to the concentration of the enzyme. With constant enzyme concentration, the decolorising power rose at first quickly with the succinate concentration, but then approached a limiting value. G. W. R.

Aliphatic Arsinic Acids, and Aliphatic-aromatic Arsenious Acids. A. J. QUICK and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1922, 44, 805—816).—Alkylarsinic acids may readily be prepared by heating together an aqueous solution of sodium arsenite and the requisite alkyl bromide or chloride. The method has been applied to the preparation of several alkylarsinic acids as well for allyl- and benzyl-arsinic acids. For the preparation of dialkylarsinic acids, the necessary alkylchloroarsine is dissolved in sufficient 10*N*-sodium hydroxide to produce the disodium alkyl arsenite and then the alkyl bromide is added and the mixture is heated under a reflux condenser. In this way, diethylarsinic acid, *propylbutylarsinic acid*, m. p. 127—128°, and *dibutylarsinic acid*, m. p. 137—138°, giving a light blue copper salt, have been obtained. For the aliphatic-aromatic arsinic acids the dichloroarsine is dissolved in alkali as described above and the alkyl or aryl haloid added at the ordinary temper-

ature, the reaction taking place rapidly. In this way a number of compounds having the general formula $\text{NHR}'\cdot\text{CO}\cdot\text{CH}_2\cdot\text{AsRO}_2\text{H}$ have been obtained, where R is a phenyl, *p*-aminophenyl, or *p*-acetylaminophenyl group, and R' is a phenyl or substituted phenyl group. The compounds described are: *Phenylarsinoacetic acid*, m. p. 141—142° (decomp.); *phenylchloroarsineacetic acid* $\text{AsPhCl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, m. p. 102—103°; *phenylbromoarsineacetic acid*, m. p. 113—114°; *phenylarsinoacetanilide*, m. p. 182—183° (decomp.); *phenylbromoarsineacetanilide*, m. p. 108—110°; *phenylarsinoacetophenetidine*, m. p. 175° (decomp.); *phenylarsinoacetoarsanilic acid*; *phenylarsino-o-acetylaminobenzoic acid*, m. p. 198—200° (decomp.); *phenoxyethylphenylarsinous acid*, m. p. 122—123°; *ethylenediphenyldiarsinous acid*, m. p. 209—211°; *p*-aminophenyldichloroarsine hydrochloride; *p*-aminophenylarsinoacetanilide, m. p. 181—182° (decomp.); *p*-acetylaminophenylarsinoacetanilide, m. p. 205—206° (decomp.); *p*-glycylaminophenylarsinoacetanilide, m. p. 199° (decomp.); *p*-aminophenylarsinoacetophenetidine, m. p. 211·5—212·5°; *p*-acetylaminophenylarsinoacetophenetidine, m. p. 214—215° (decomp.); *p*-aminophenylarsinoacetoarsanilic acid; *p*-acetylaminophenylarsinoacetoarsanilic acid; *p*-aminophenylarsino-*p*-acetylaminobenzoic acid, m. p. 217° (decomp.).

Butyldichloroarsine, b. p. 192—194°, is obtained by the action of sulphur dioxide on butylarsinic acid in hydrochloric acid solution in the presence of a little potassium iodide. *p*-Chloroacetylaminobenzoic acid, m. p. 239°, is obtained by the action of chloroacetyl chloride on *p*-aminobenzoic acid.

The arsenic derivatives described above dissolve readily in aqueous alkalis, giving solutions which have relatively low toxicity but at the same time only a slight trypanocidal action. W. G.

The Sulphur Content of Arsphenamine (Salvarsan) and its Relation to the Mode of Synthesis and the Toxicity. I. WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1922, **44**, 847—854; cf. this vol., i, 186; Fargher and Pyman, T., 1920, **117**, 370).—The total sulphur content of salvarsan was found to vary from 0·4% up to 3%, according to the method of preparation, and those preparations which contained the highest percentage of sulphur were the most toxic. There was no direct relationship, however, between these two factors. Only the sulphur in excess of that introduced when 3-nitro-4-hydroxyphenylarsinic acid is reduced by hyposulphite under the most favourable conditions has any great effect on the toxicity. The sulphonic acid of salvarsan, described by King (T., 1921, **120**, 1107, 1414), could only be isolated from salvarsan preparations made from the nitro-acid under the least favourable conditions. The presence of this sulphonic acid cannot account for the whole of the high toxicity which is obtainable. W. G.

The Sulphur Content of Arsphenamine (Salvarsan) and its Relation to the Mode of Synthesis and the Toxicity. II. WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1922, **44**, 854—859; cf. preceding abstract).—Highly toxic salvarsan preparations

with high sulphur content prepared by the hyposulphite reduction of 3-nitro-4-hydroxyphenylarsinic acid differ from those obtained from known mixtures of 3-amino-4-hydroxyphenylarsinic acid and its 5-sulphonic acid (cf. King, T., 1921, 120, 1107, 1414) in several points, such as the rate at which the sulphonic acid separates from the alcohol solution, the effect of temperature on the formation of the precipitate, the ease of separation of the precipitate from the mother-liquor, and the rate of death of rats when the preparations are injected intravenously. These differences, it is suggested, may be due to heating causing a rearrangement of some unstable substance or to an alteration in colloidal properties. W. G.

Lead Triaryl, a Parallel to Triphenylmethyl. III. Lead Triphenyl, Tri-*p*-tolyl and Tri-*o*-tolyl and Dark Red Lead Diaryls. ERICH KRAUSE and G. G. REISSAUS (*Ber.*, 1922, 55, [B], 888—902).—In continuation of the work on lead tri-*p*-xylyl (Krause and Schmitz, A., 1920, i, 197) and lead tricyclohexyl (Krause, A., 1921, i, 825), the lower homologues are now described; it has also been found possible to isolate certain intermediately formed lead diaryls in the homogeneous condition. The latter are intensely coloured, dark red, apparently amorphous powders which give blood-red solutions in benzene or ether from which they are precipitated unchanged by alcohol. In freezing benzene they have the simple molecular weight, and hence are shown definitely to be derivatives of bivalent lead. They are highly unsaturated. In the solid state or in solution, they readily absorb atmospheric oxygen, becoming decolorised and transformed into derivatives of quadrivalent lead. They combine instantly with iodine and reduce silver nitrate to metallic silver. On the other hand, when isolated they are comparatively stable and retain their red colour for weeks if carefully shielded from light and air. They are very analogous to the tin diaryls (Krause and Becker, A., 1920, i, 340) but are considerably less stable than these substances. When heated alone or in solution, they undergo complex decomposition, whereas in the presence of an excess of magnesium aryl bromide they are converted smoothly and readily into lead triaryls.

Lead triphenyl is remarkable for its close resemblance to hexaphenyldistannan (Krause and Becker, *loc. cit.*); in the solid condition it is probably bimolecular, but the designation "hexaphenyldiplumban" does not appear to be appropriate, since it has the simpler molecular weight in dilute solution. This is also true of the tri-*p*-tolyl, tri-*o*-tolyl, and tri-*p*-xylyl compounds. The lead triaryls show remarkable differences in the ease with which they pass into tetra-aryls; this occurs very readily with the phenyl compounds, more difficultly with the *p*-tolyl derivative, whereas it is not possible with the *o*-tolyl or *p*-xylyl compounds.

The following individual substances have been prepared by the action of the requisite magnesium aryl haloid on lead chloride in the presence of ether or benzene. It is remarkable that the yields appear to depend to a not inconsiderable extent on the origin of

the lead chloride. The success of the experiments is governed greatly by exact adherence to experimental conditions, which are described fully in the original. *Lead diphenyl*, a blood-red, amorphous powder which is decolorised and decomposed at about 100°, becomes yellow at 120° and melts above 200°, without, however, blackening below 260°. *Lead di-p-tolyl*. *Lead triphenyl*, almost colourless, lustrous rhombohedra (C_6H_5)₃ from benzene, pale yellow, rhombic platelets from chloroform, incipient decomp. 155° and m. p. 225° (m. p. of lead tetraphenyl); it is converted into lead tetraphenyl when heated alone (see above), in benzene solution at 100°, or in pyridine solution at 60–65°; its solution in benzene is converted by an aqueous alcoholic solution of iodine into lead triphenyl iodide and by a dilute solution of iodine in benzene into lead iodide, together with a little lead diphenyl diiodide. *Lead tri-p-tolyl*, hexagonal platelets or rhombohedra, decomp. 193° and subsequent m. p. 240° (m. p. of lead tetra-p-tolyl); in contrast to lead tri-p-xylyl and lead tricyclohexyl, it is converted by bromine in freezing pyridine into lead bromide and lead tetra-p-tolyl, thus pointing to the possible existence in pyridine solution of the equilibrium $2\text{Pb}(\text{C}_6\text{H}_4)_3 \rightleftharpoons \text{Pb}(\text{C}_6\text{H}_4)_4 + \text{Pb}(\text{C}_6\text{H}_4)_2$; with iodine in the presence of water, it gives *lead tri-p-tolyl iodide*, m. p. 115°, decomp. about 195°. *Lead tri-o-tolyl*, microscopic rhombohedra which deposit lead at about 240° and melt to a black liquid at about 250°. *Lead tri-p-xylyl chloride* crystallises in silvery, rectangular plates, m. p. 167.5°, decomp. about 195°.

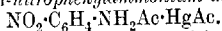
H. W.

The Nitroanilines. MORRIS S. KHARASCH, FREDERICK W. M. LOMMEN and ISADORE M. JACOBSON (*J. Amer. Chem. Soc.*, 1922, **44**, 793–805).—Evidence is adduced in support of the nitronic structure of *o*- and *p*-nitroanilines, and it is considered that in alcoholic solution they exist in two or more tautomeric forms (cf. Baly, Edwards, and Stewart, T., 1906, **89**, 517). In alcoholic solution they give with mercuric acetate intensely coloured mercury salts, whereas with *m*-nitroaniline the reaction is only slow and the product is almost white. Using nascent mercuric oxide, Jackson and Peakes (A., 1908, i, 523) obtained highly coloured compounds with all three isomerides, but it is shown that their compound obtained from the meta-isomeride is only an additive compound, as, on extraction with acetone, the whole of the nitroaniline is removed and only the mercuric oxide is left. The *o*- and *p*-salts, when similarly extracted, remain unchanged. The authors suggest a formula for *p*-nitrodimethylaniline, in which its nitronic structure is retained, which should overrule Baly's objections (cf. T., 1910, **97**, 581). The mechanism of mercurisation is discussed and three possible ways in which *o*- and *p*-nitroanilines might be mercurised are suggested. The positions taken by the entering mercury in the nitroanilines has been established as ortho or para or ortho-para to the amino-group. This has been shown by acetylation and subsequent replacement of the mercury by bromine.

o-Acetoxymercuri-*p*-nitroaniline is best obtained by the interaction of mercuric acetate and *p*-nitroaniline in alcoholic solution. With hydrochloric acid it yields *o*-chloromercuri-*p*-nitroaniline, and with sodium thiosulphate it gives *o*:*o*'-mercury-bis-*p*-nitroaniline. With dilute sodium hydroxide or carbonate, the acetoxy- or chloro-derivatives give quinone-1-imide-*aci*-4-nitro-2-mercury. If, in the preparation of the acetoxy-derivative, an excess of mercuric acetate is used *o*:*o*'-diacetoxymercuri-*p*-nitroaniline is obtained. On acetylation the acetoxy-derivative yields *o*-acetoxymercuri-*p*-nitroacetanilide, which on bromination gave *p*-nitro-*o*-bromoacetanilide.

Similar derivatives were prepared from *o*-nitroaniline as follows: *p*-acetoxymercuri-*o*-nitroaniline; *p*-chloromercuri-*o*-nitroaniline; quinone-1-imide-*aci*-2-nitro-4-mercury; *p*-acetoxymercuri-*o*-nitrodiacetanilide; *p*-acetoxymercuri-*o*-nitroacetanilide.

m-Nitroaniline reacts with mercuric acetate in alcohol to give *N*-isomercuriacetate-*m*-nitrophenylammonium acetate,



By varying the conditions and the quantities of the reacting substances *o*:*p*-diacetoxymercuri-*m*-nitroaniline and *p*-acetoxymercuri-*m*-nitroaniline are obtained, the latter yielding *p*-acetoxymercuri-*m*-nitroacetanilide on acetylation.

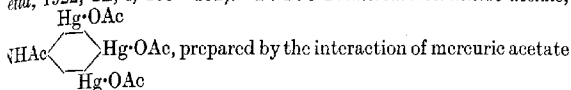
W. G.

Organic Nitro-compounds containing Mercury. GEORGE W. RAIZISS and A. PROSKOURIAKOFF (*J. Amer. Chem. Soc.*, 1922, **44**, 787—793).—In the case of nitrophenol and nitrosalicylic acid, the introduction of mercury into the nucleus is effected by warming the compound with either mercuric acetate or oxide in water for several hours. A mixture of mono- and di-mercurated products usually results. The corresponding chloromercuri-compounds may be obtained by the action of hydrochloric acid. The authors obtained such a mixture from *o*-nitrophenol, their results thus disagreeing with those of Hantsch and Auld (cf. A., 1906, i, 471). With 5-nitrosalicylic acid, the dimercury derivative is obtained almost exclusively, even although allowed to react with only equimolecular quantities of mercuric oxide or acetate. The biological properties of these compounds have been examined, and of the entire number sodium hydroxymmercuri-*o*-nitrophenoxide was found to be far superior to the others. The following compounds are described: 4-chloromercuri-2-nitrophenol; sodium hydroxymmercuri-*o*-nitrophenoxide (mercurophen) (cf. *J. Infect. Diseases*, 1919, **24**, 547); 2-chloromercuri-4-nitrophenol; 4-acetoxymercuri-2-nitroresorcinol; 4-chloromercuri-2-nitroresorcinol; 3-chloromercuri-5-nitrosalicylic acid, m. p. 238° (decomp.); diacetoxymercuri-5-nitrosalicylic acid. The mercurisation of 3-bromo-5-nitrosalicylic acid and of 3:5-dinitrosalicylic acid gave mixtures of mono- and dimercury compounds from which it was not possible to separate pure substances. None of the compounds described above were affected by ammonium sulphide at room temperature within thirty minutes (cf. A., 1920, i, 196).

Modifications in the preparation of 5-nitro- and 3:5-dinitrosalicylic acids are described.

W. G.

Colloidal Trimercuriacetanilide Acetate. G. ROSSI (*Gazzetta*, 1922, 52, i, 189—192).—2 : 4 : 5-Trimercuriacetanilide acetate,



and acetanilide at 140°, forms a friable, vitreous mass and softens and decomposes at above 180°. It dissolves slowly but abundantly in water, yielding colloidal solutions which froth when shaken, coagulate when heated, and are incapable of dialysis; in these properties, the compound resembles the corresponding tetra- and pentamercuriacetanilide acetates (cf. Raffi and Rossi, A., 1912, i, 931; 1914, i, 610). With these three acetates, the colloidal properties become more clearly marked as the molecular weight increases. Treatment of trimercuriacetanilide acetate in aqueous solution with excess of bromine dissolved in potassium bromide solution results in the formation of 2 : 4 : 5-tribromoacetanilide. T. H. P.

Preparation of Esters of Complex Mercuridicarboxylic Acids and their Products of Hydrolysis. WALTER SCHOELLER and WALTHER SCHRAUTH (D.R.-P. 339494; from *Chem. Zentr.*, 1921, iv, 1224).—Esters of sulphido-mercuridicarboxylic acids are heated, whereby mercuric sulphide is split off; the resulting esters may be hydrolysed (cf. Schoeller, Schrauth, and Hueter, A., 1920, i, 455—456). Methyl sulphido-dimercuri-*o*-acetylamidobenzoate, prepared by the action of freshly prepared alcoholic hydrogen sulphide on methyl acetoxy-mercuriacetylanthranilate, is heated at 80—100° until 1 molecule of mercuric sulphide is split off. The resulting methyl mercuridiacetylamidobenzoate is separated by solution in acetone and filtration from the mercuric sulphide. It has a light yellow colour and m. p. about 200° with previous discoloration. Ethyl mercuridisalicylate is similarly prepared; it is a crystallisable oil. Methyl mercuridibenzoate, prepared by way of the sulphidomercuribenzoate, is a white, microcrystalline compound. By hydrolysis, it gives an amorphous substance, containing 45.07% of mercury, identical with the mercuridibenzoic acid of Pesci (A., 1901, i, 624). Ethyl sulphido-mercurimethoxybutyrate, from ethyl acetoxymercurimethoxybutyrate (itself obtained from the action of mercuric acetate on ethyl crotonate) gives on heating ethyl α -mercuridi- β -methoxybutyrate obtained as microcrystalline needles by recrystallisation. α -Mercuridi- β -methoxybutyric acid is obtained by hydrolysis as a white, amorphous powder. G. W. R.

Physiological Chemistry.

Estimation of the Relative Numbers of Red Blood-corpuscles of Differing Resistance (Osmotic Resistance Curves) by means of Sodium Sulphate. H. J. HAMBURGER (*Biochem. Z.*, 1922, 129, 163—182).—Corpuscles washed with isotonic sodium sulphate solution lose their adsorbed lecithin layer and when exposed to solutions of sodium sulphate of increasing concentration show a curve of resistance to hæmolysis different from that of unwashed corpuscles. Washed corpuscles are more resistant than unwashed. It is shown that regeneration of blood after anæmia due to blood-letting in rabbits is most rapid if lecithin and fatty foods be consumed. H. K.

The Dextrose Content of the Red Blood-corpuscles of Man and their Behaviour in Isotonic Sugar Solutions. M. BÖNNIGER (*Biochem. Z.*, 1922, 128, 482—486).—The red blood-corpuscles of man, when kept in isotonic dextrose solution at 0°, 15°, or 37°, show a considerable increase in volume after one hour, especially at the higher temperatures. When kept longer, those at 0° decrease in volume, whilst those at 15° and 37° continue to increase and finally those at 37° show hæmolysis. The corpuscles of sheep and guinea pigs always diminish in volume independently of the temperature. H. K.

The Importance of Potassium and Calcium Ions for the Production of Artificial Œdema and for the Width of the Blood Vessels. RUDOLF J. HAMBURGER (*Biochem. Z.*, 1922, 129, 153—162).—Potassium can be omitted from a perfusion fluid for a frog's limb without production of œdema if the solution contain 0.6% NaCl and 0.007% $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. Addition of 0.01% KCl or a fall of concentration of the calcium chloride to 0.006% produced œdema. Higher concentrations of calcium chloride, for instance, 0.01% constrict the blood-vessels so that no fluid will pass, but on addition of a little potassium chloride the flow recommences. The action is reversible. The action of the calcium ion is to constrict the capillaries and to cause a thickening of their walls, a property also possessed by solutions saturated with oxygen. H. K.

The Sterilisation of the Intestine during Fasting. STEFAN DOMBROWSKI and (the late) STANISLAS KOZŁOWSKI (*Bull. Soc. Chim. Biol.*, 1922, 4, 71—79).—Fasting, accompanied by daily washings with tepid water to eliminate faeces remaining from the period preceding the fast, produces an advanced sterilisation of the intestine. From the fourth day, the excretion of conjugated sulphuric acid and of indican in the urine is at a minimum, whilst bilirubin and cholesterol undergo no change in the intestine, but are excreted as such in the faeces. E. S.

The Rôle of Ketonic Compounds in Intermediate Exchanges and in the Formation of Sugar from Fat. H. CHR. GEELMUYDEN (*Skand. Arch. Physiol.*, 1921, 40, 211—225; from *Chem. Zentr.*, 1921, iii, 1508—1509).—Oil was injected into the stomach of rabbits poisoned with phloridzin. The elimination of sugar rose at once and remained high for several days. The increase in sugar was not, however, in excess of that to be expected from the amount of oil administered. Phloridzin-diabetic dogs excrete "extra sugar" after subcutaneous injection of sodium acetate and sodium butyrate, but not in the case of sodium *n*-hexoate. Strongly diabetic men show, after administration of "ketogenous" amino-acids (*isovaleric acid*, tyrosine, phenylalanine, *d*-leucine, and butyric acid), increased excretion of sugars and ketonic compounds. Ketonic compounds and sugar may be formed on the one hand from fats and their derivatives and on the other from the amino-acids of proteins. Ketonuria must be considered as a sign of defective or incomplete sugar synthesis. G. W. R.

Physical Chemistry of Colour Vision. FRITZ WEIGERT (*Z. physikal. Chem.*, 1922, 100, 537—565).—A theoretical paper in which the physical chemistry of the mechanism of colour vision is discussed. J. F. S.

Odour and Chemical Structure. H. ZWAARDENAKER (*Arch. Neerland. physiol.*, 1922, 6, 336—354).—The intensity of the odour of a substance is an additive property, depending on such physical properties as volatility and solubility in lipoids; the quality of the odour is a constitutive property, depending on the presence in the molecule of certain specified groupings, designated "odoriphores," and on the magnitude and number of the groupings in the molecule and their intra-molecular arrangement. Thus attention is directed to the regular transition in the type of odour observed in ascending certain homologous series of compounds.

With reference to the theory that odour is due to intra-molecular movements, it is pointed out that these movements are themselves determined by the above-mentioned factors. C. R. H.

The Rôle of Vitamins in the Chemistry of the Cell. EMIL ABDERHALDEN (*Z. physiol. Chem.*, 1922, 119, 117—120).—The author points out that he had published conclusions similar to Hess (this vol., i, 399) on the relation of the antineuritic vitamin to cell oxidation processes. W. O. K.

Chemical Conditions for the Maintenance of Normal Cell Structure. IV. Difference in Nitrogen and Water Content of Muscle treated with Sodium and Calcium Chloride. ERIK M. P. WIDMARK and GUNNAR LINDAHL (*Skand. Arch. Physiol.*, 1921, 41, 221—226; from *Chem. Zentr.*, 1921, iii, 1367—1368; cf. Widmark, A., 1911, ii, 56).—The extraction of rabbit muscle by solutions of sodium chloride, and sodium chloride together with calcium chloride, respectively, was studied. The nitrogenous substances extracted amounted to 15—20% of the weight of tissue used. There was no marked difference between the amount

extracted by the two solutions. In the case of the solution containing calcium chloride, however, the water content of the tissue was lowered, probably owing to dehydration of tissue colloids. The effect of calcium ions on muscle is attributed to this rather than to extraction of proteins.

G. W. R.

Chemical and Physical Properties of Muscle and Muscle Extracts. VI. Muscle Extract of Octopus. G. QUAGLI-ARIELLO (*Arch. internat. Physiol.*, **16**, 228—238; from *Chem. Zentr.*, 1921, iii, 1368; cf. A., 1921, i, 831).—Muscle extract from octopus has d_{20}^{25} 1.051; it is slightly acid in reaction and shows under the ultramicroscope, particularly on dilution with 3.5% sodium chloride solution, great numbers of myosin granules in energetic Brownian motion. The relative viscosity is 5.09; relative conductivity at 18°, 0.0233 reciprocal ohm; surface tension (by stalagmometer), 0.68. The opalescence increases above 38°, and at 54—55° coagulation takes place. The extract contains 85.8% of water, 3.02% of ash, 1.626% of total nitrogen, and 0.374% of residual nitrogen.

G. W. R.

Calcium Fixation by Animal Tissues. VII and VIII. E. FREUDENBERG and P. GYÖRGY (*Biochem. Z.*, 1922, **129**, 134—137; 138—143).—VII.—The ultra-filtration of calcium from a serum solution is accelerated by addition of potassium chloride more than by nitrate, acetate, phosphate, or hydrogen carbonate. Anions also influence the swelling of cartilage, the imbibition being greater for calcium chloride than nitrate or acetate. Fixation of calcium is inhibited by creatine or ethylamine.

VIII.—Formaldehyde and dextrose inhibit fixation of calcium by cartilage, but ethyl alcohol and acetone in decinormal solution are without action. Calcium fixation is accelerated by rise of temperature.

H. K.

Dyeing of Deaminated Wool. W. W. PADDON (*J. Physical Chem.*, 1922, **26**, 384—389).—Ordinary white wool, and the same material which had been deaminated by treating with nitrous acid at 4° and subsequently boiling, has been dyed by orange II and lake scarlet-R and the amount of dye removed from the bath determined. The change in the P_H value at the end of the operation was also determined. The P_H values have been plotted against the quantity of dye removed, and curves very similar in shape and position obtained; the differences between the two curves could well be attributed to experimental errors. The results show that the amino-groups in wool play no part whatever in the dyeing of that fibre by acid dyes.

J. F. S.

Toxin of the Fish, *Plotosus anguillaris*. I. KABESHIMA (*Nippon Biseibutsugakki Zasshi*, 1918, **6**, 45—270; *Jap. Med. Literature*, 1920, **5**, 23—24).—Plototoxin, a poison occurring in the fish, *Plotosus anguillaris*, consists of two active substances, *plotospasmin* and *plotohemolysin*, which may be separated by

adsorption methods. The experimental work is concerned with the physiological behaviour of these two substances, and with the effect of heat, light, and shaking on their potency.

CHEMICAL ABSTRACTS.

Fatty Matters in the Sea Urchin. KATSUMI TAKAHASHI (*J. Chem. Soc. Japan*, 1922, **43**, 243—257).—Analysis of the sea urchin gave: water 45.31%, dry substance 54.69%, total nitrogen 2.43%, crude fat 12.91%, crude ash 13.22%, and phosphorus 0.41%. The crude fatty matter contained lecithin 19.628%, cephalin 1.736%, cholesterol 5.585%, and fat 73.051%. The fat gave 19.181% of saturated acids (mainly palmitic acid, with small quantities of stearic or myristic acid) and 53.870% of unsaturated acids which gave four bromides containing 66.26%, 61.20%, 55.25%, and 43.57% of bromine, respectively. The properties and composition of the lecithin and cephalin were in good agreement with those from the hen's egg.

K. K.

Presence of Aromatic Hydroxy-acids in Urines. G. DE SANCTIS and Q. FIORI (*Boll. Chim. Farm.*, 1922, **61**, 97—102).—The authors discuss this subject and describe the isolation of hydroparacoumaric or β -*p*-hydroxyphenylpropionic acid from the urine of a patient to whom no aromatic medicaments had been administered by ingestion. The acid is derived from the tyrosine of food under the influence of intestinal putrefaction. T. H. P.

Hæmatoporphyrin in the Urine in Cases of Lead Poisoning. O. SCHUMM (*Z. physiol. Chem.*, 1922, **119**, 139—149).—On examining several samples of urine from patients suffering from lead poisoning, it was found that a hæmatoporphyrin identical with the hæmatoporphyrin from fæces, or one resembling it very much, was present either alone or in preponderance in the urine.

S. S. Z.

Estimation of Urinary Colloids by the Gold Number. B. OTTENSTEIN (*Biochem. Z.*, 1922, **128**, 382—390).—The author has determined the gold number of dialysed urine containing colloids both of normal persons and of pathological cases. In normal urine, the gold number varies between 7 and 3.5, and is independent of the reaction of the urine. In pathological cases, there is considerable variation.

H. K.

The Proteolytic Enzymes in Albuminous Urines. S. G. HEDIN (*Z. physiol. Chem.*, 1922, **119**, 264—279).—Strongly albuminous urine, when previously kept acid, digests its protein or added casein in alkaline solution more readily than when it is previously kept in weakly alkaline solution. It is suggested that the urine contains an inhibitory substance which is decomposed by acid. The action of trypsin on casein and peptone is inhibited to a greater extent by the addition of urine previously kept alkaline than by that of urine previously kept acid.

S. S. Z.

VOL. CXXII. i.

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Chromic Acid Nephritis. R. H. MAJOR (*Bull. Johns Hopkins Hosp.*, 1922, 33, 56—61).—A fatal case of nephritis, consequent on the cauterisation of a wound with chromic acid, is described. The maximum concentrations in the blood, expressed as mg. per 100 c.c., were: non-protein nitrogen, 373; urea nitrogen, 340; creatinine, 17; creatine, 19; uric acid, 9; sugar, 220. The plasma carbon dioxide capacity fell to 31%, and the plasma chlorine remained low, about 400 mg. per 100 c.c.

CHEMICAL ABSTRACTS.

Physiological Action of Proteinogenic Amines. V. J. ABELIN (*Biochem. Z.*, 1922, 129, 1—49).—Experiments on rats show that substances such as tyramine, phenylethylamine, adrenaline, choline, pilocarpine, and atropine, which stimulate the vegetative nervous system, influence the metabolic processes. There is increased gaseous metabolism, mobilisation of glycogen, hyperglycaemia and glycosuria, and increased excretion of urine. Tyramine and phenylethylamine reinforce the action of each other, and, in conjunction with small quantities of thyroid preparations which in themselves are inactive, produce a strong increase in the gaseous metabolism. Histamine has no influence on the gaseous metabolism, whilst acetylcholine depresses it.

H. K.

The Cinchona Alkaloids. H. W. ACTON (*Lancet*, 1922, i, 124—128; from *Physiol. Abstr.*, 1922, 7, 58).—The “cinchonine series”—cinchonine, cupreidine, and quinidine—which are dextro-rotatory are more powerful in their physiological action than their levorotatory isomerides of the “cinchonidine series”—cinchonidine, cupreine, and quinine. The hydroalkaloids are more stable and in many respects more active than the natural alkaloids. Of the alkyl-hydroalkaloids, the higher members are more toxic than the lower members to mammals, protozoa, and bacteria.

W. O. K.

Surface Activity and Toxic Action of Saponins. LUDWIG KOFLER (*Biochem. Z.*, 1922, 129, 64—72).—The author has measured the hæmolytic index, the drop number, and the fish index (the concentration of substance which kills a young roach, 0.1—0.5 gram in one hour) of eight saponins. There is no parallelism in these properties. The order of the drop numbers may even change with change in the concentrations studied. It is considered essential that in order to trace the relation between the surface activity and the physiological action, the concentration used in the surface tension measurements should be that used in the physiological experiment.

H. K.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Arsenious Acid on Bacterial Growth. R. COBET and V. VAN DER REIS (*Biochem. Z.*, 1922, **129**, 73—88).—No evidence was found that arsenious acid could stimulate the growth of bacteria. H. K.

Influence of Lactic Acid on Lactic Acid Fermentation. B. J. HOLWERDA (*Biochem. Z.*, 1922, **128**, 465—481).—As the result of conductivity measurements and colorimetric measurements on lactic acid and of potentiometric measurements on mixtures of lactic acid and sodium or calcium lactate, the dissociation constant of lactic acid is found to be 1.5×10^{-4} at 25°. Bredig's diazoacetic ester method gives values for the dissociation constants of organic acids which are 8 to 10% too low. Lactic acid fermentation in a whey containing peptone is inhibited by undissociated lactic acid. H. K.

Zymase Formation in Yeast. I. F. HAYDUCK and H. HAEHN (*Biochem. Z.*, 1922, **128**, 568—605).—The distribution of zymase in bottom beer-yeast and in distillery yeast is different. Bottom beer-yeast contains free zymase and zymase combined with protoplasm, the former zymase alone being active after treatment of such yeast by Lebedev's process or in yeast fixed by acetone, even in the presence of toluene. Distillery yeast, which gives no active press juice or active zymase after acetone fixation, contains only combined zymase, its activity being inhibited by toluene owing to formation of impermeable emulsions with the lipid membranes of the cells. Experiments on a torula yeast poor in zymase showed that cultivation in a wort with a weak air supply caused an increased content of zymase and parallel with this an increased nucleic acid metabolism. The differences observed in the two first-named yeasts is attributed to differences in their mode of living. H. K.

A New Acid Fermentation produced by *Sterigmatocystis nigra*. MARIN MOLLIARD (*Compt. rend.*, 1922, **174**, 881—883).—When *Sterigmatocystis nigra* [*Aspergillus niger*] is grown on a medium very poor in nitrogen and mineral salts the main, and in some cases the only acid produced is *D*-glucosic acid. If only the nitrogen is low in the medium then citric acid predominates in the products, but if phosphorus is the nutrient which is lacking there is marked acidity produced, due in this case to a mixture of citric and oxalic acids. If, on the other hand, potassium is the missing nutrient, then there is an accumulation of oxalic acid. On a properly balanced medium only traces of free acid are produced. W. G.

A New Antiseptic with High Iodine Content. (Diethylene Disulphide Tetraiodide.) C. BACHEM (*Biochem. Z.*, 1922, **129**, 190—193).—The properties of diethylene disulphide tetraiodide,

$\text{SI}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{SI}_2$, containing 81% of iodine have been examined with a view to its use as a wound antiseptic. Its most striking action is its powerful inhibitory action on bacterial growth. It is not decomposed by proteins, is relatively non-toxic to rabbits, but has a disagreeable odour. The iodine is liberated slowly by water and completely by ether.

H. K.

Relationships between Antiseptic Action and Chemical Constitution, with Special Reference to Compounds of the Pyridine, Quinoline, Acridine, and Phenazine Series. C. H. BROWNING, J. B. COHEN, R. GAUNT, and R. GULBRANSEN (*Proc. Roy. Soc.*, 1922, [B], 93, 329—366).—The bactericidal action of derivatives of pyridine, quinoline, acridine, and phenazine on *Staphylococcus aureus* and on *Bacillus coli* has been investigated. In the pyridine, quinoline, and phenazine series no compound has been found possessing an activity equalling that of certain diaminoacridine derivatives, particularly in presence of serum which inhibits their efficiency. In the acridine group, the introduction of amino-groups enhances the antiseptic potency, and this effect is in general weakened again by alkylation or acetylation, or replacement by hydroxyl. The methochloride is equal to or better than the hydrochloride of the same base. Substitution of the methyl group by another radicle is without much effect. The carboxyl group seems to depress the antiseptic property. The comparative efficiencies for *S. aureus* and *B. coli* do not invariably run parallel.

The following new compounds have been prepared. α -Dimethylaminopyridine methiodide, fine, colourless needles which turn yellow in the air; dinitro- β -naphthaquinoline, m. p. 245—247°; diamino- β -naphthaquinoline, pale yellow plates, m. p. 250°; 2:7-diacetyldiaminoacridine chloroacetate, yellow crystals; 2:7-diaminoacridine chloroacetate, red crystals; 2:7-diaminoacridine chloroacetanilide, brown crystals; 2-amino-9-phenyl-3-methylnaphthacridine, yellow needles, m. p. 269—271°; 7-amino-2-dimethylamino-6-methylphenazine methochloride, microcrystalline powder with dark green lustre; 2-dimethylamino-6-methylphenazine methiodide, brownish-black plates; N-methyltetrahydroquinoline-2-aminophenazine methochloride, green, iridescent mass (zinc salt).

W. O. K.

The Relation between Chemical Constitution and Antiseptic Action in the Coal Tar Dyes. THOMAS H. FAIRBROTHER and ARNOLD RENSHAW (*J. Soc. Chem. Ind.*, 1922, 41, 134—144).—The action of numerous dyes on cultures of paramœcia and of various bacteria was examined.

It was found that efficient antiseptic action was dependent on the presence in the molecule of free amino-groups, but that the effect of these was neutralised by the presence of sulphonic, carboxyl, nitro-, and naphthylamino-groups. The most actively antiseptic dyes were those of the triphenylmethane series and the oxazines. The triphenylmethane dyes were especially active in the simple salt form and in the form of a double salt with a metallic

salt of the same acid as the dye (for example, crystal-violet zinc chloride). Some of the dyes possessed a selective action; thus the oxazines in general killed gram-positive organisms and left the gram-negative ones unaffected.

Antiseptic activity is associated with the possibility of tautomeric change in the molecule, and with the existence of the substance in the molecular dispersoid form. It does not vary with intensity of colour or with molecular weight.

C. R. H.

Influence of Selenium and Radium on the Germination of Seeds. J. STOKLASA (*Compt. rend.*, 1922, 174, 1075—1077).—Both selenites and selenates exert a markedly injurious influence on the germination of seeds. Selenates are much less toxic than selenites, and at great dilution even exert a favourable influence. This injurious action of selenium compounds is to a large extent neutralised by the radioactivity of the medium. In the absence of selenium compounds, the germinative energy of seeds is considerably increased by water charged with radioactive emanation.

W. G.

Studies on Photosynthesis. IV. Carbon Dioxide Assimilation by Leguminosae. S. KOSTYTSCHEV (*Ber. Deut. bot. Ges.*, 1922, 40, 112—119; cf. this vol., i, 307, 308).—In gasometric experiments with the concentration of carbon dioxide above that in the atmosphere, carbon dioxide assimilation by Leguminosae is markedly greater than by other plants. The presence of nitrates in the soil increases the assimilation; the effect is, however, not shown in short period experiments. Alder species although possessing nodules on their roots do not resemble the Leguminosae in their energy of carbon dioxide assimilation.

G. W. R.

Aluminium Salts and Acids at Varying Hydrogen-ion Concentrations, in Relation to Plant Growth in Water Cultures. S. D. CONNER and O. H. SEARS (*Soil Sci.*, 1922, 13, 23—41).—The results of the investigation showed that the toxicity of aluminium salts is due to the aluminium-ion more than it is to the hydrogen-ion in the case of such plants as barley and that this toxicity is reduced when much phosphate is present in the nutrient medium. Acid soils are toxic to many plants mainly because they contain readily soluble aluminium salts.

W. P. S.

The Part Played by Lipoids in the Metabolism of Plant Cells. II. FRIEDRICH BOAS (*Biochem. Z.*, 1922, 129, 144—152).—The action of solanine, bile acids, urethane, quinine, and cocaine has been examined on the fermenting capacity of yeast-cells. Saponaceous substances like solanine and the bile acids, in presence of neutral salts, have an inhibitory action attributed to a change of the lipid structure of the cell, causing increased permeability. Quinine and cocaine were found to promote fermentation.

H. K.

Influence of Selenium on Plant Evolution in the Presence or Absence of Radioactivity. J. STOKLASA (*Compt. rend.*, 1922, 174, 1256—1258).—Sodium selenate at a concentration of 5×10^{-6} up to 10^{-5} gram-atoms of selenium per litre produces a stimulating effect on the growth of maize, but at higher concentrations it is toxic. Selenites are more toxic than selenates. This injurious action of selenium compounds is almost completely neutralised by the presence of radium emanation to the extent of 0.0000056 mg. per plant. Selenium dioxide is much more toxic than sulphur dioxide towards plants.
W. G.

Absorption of Ions by the Roots of Living Plants. I. Absorption of the Ions of Calcium Chloride by Pea and Maize. GLADYS M. REDFERN (*Ann. Bot.*, 1922, 36, 167—174).—Seedlings of pea and maize grown in culture solutions were transferred to solutions of calcium chloride of varying concentration. The percentage absorption of calcium is in every case greater than the percentage absorption of chlorine, the difference being less in the most dilute solutions used (0.001N). The P_{11} remains approximately constant, potassium and magnesium diffusing from the roots and presumably replacing the calcium absorbed. Equilibrium is reached in the intake of this salt within the first twenty-four hours in the case of peas and within the first forty-eight hours in the case of maize. No trustworthy evidence of periodicity in absorption was obtained.
G. W. R.

The Genesis of Amylase and Maltase in Plants. W. PALLADIN and HELENE POPOV (*Biochem. Z.*, 1922, 128, 487—494).—In green and etiolated leaves of various plants, some diastase remains fixed by the protoplasts even after protracted autolysis and thorough percolation in water, and some passes into solution. More diastase is found fixed in young leaves than in old leaves and none is found in dead leaves.
H. K.

The Hydrocyanic Acid Question. K. SIEGFRIED (*Schweiz. Apoth. Ztg.*, 1921, 59, 325; cf. *Schweiz. Wochschr.*, 47, 541; Rosenthaler, A., 1921, i, 484; Wester, *Pharm. Weekblad*, 1914, 51, 207).—Old cherry-laurel leaves yield low percentages of hydrocyanic acid. Recent estimations in fresh leaves showed 0.253%, and in older leaves on the same branches 0.185%, both high results.

CHEMICAL ABSTRACTS.

The Hydrocyanic Acid Question. VIII.—Plants containing Hydrocyanic Acid and Saponin. IX.—Hydrocyanic Acid Content of Cherry-laurel Leaves Infected by Fungi. X.—Influence of Lesions on the Hydrocyanic Acid Content of Cherry-laurel Leaves. L. ROSENTHALER (*Schweiz. Apoth. Ztg.*, 1921, 59, 466—469; 641—643, 643—647; cf. A., 1921, i, 484).—VIII.—Of one hundred Argentinian plants examined, fourteen yield hydrocyanic acid but do not contain saponin, eighty-five contain saponin but do not yield hydrocyanic acid, whilst only one (*Manihot tucayensis*) contains saponin and also yields hydrocyanic acid.

IX.—Normal leaves had an average of 0.23 and 0.21% of hydrogen cyanide in two series; infected leaves had only 0.13 and 0.165%. In normal young sprouts, the content of hydrogen cyanide decreases with distance from the centre of growth; infected sprouts show irregular amounts.

X.—Cuts were made into half of the leaf-blade, both halves being separately examined later. Lesions made in August and September showed no increase in hydrogen cyanide content.

CHEMICAL ABSTRACTS.

Comparative Plant Chemistry. II. The Berry Fruit of some Caprifoliaceæ. GISELA NOWAK and JULIUS ZELLNER (*Monatsh.*, 1921, **42**, 293-310).—The fruit (flesh and seeds together) of the following species of Caprifoliaceæ was submitted to qualitative and quantitative chemical examination: *Lonicera xylosteum*; *L. nigra*; *Viburnum opulus*; *V. lantana*; *Sambucus nigra*; *S. racemosa*; and *Symphoricarpus racemosa*. There was found a marked general similarity among the different species which can be expressed in the following average results, calculated on the dry materials: water-soluble, 50%; invert-sugar, mainly dextrose, 25%; pectin, 3%; free acid, 3%; water-soluble inorganic salts, 3%; total ash, 4%; proteins, 7%; 1.5% waxy substances, small quantities of tannin. There are several fairly wide variations from the mean, for example *Symphoricarpus racemosa* has about 55% invert-sugar and *Sambucus racemosa* gave about 30% of fatty oil, which in this case only is contained in the flesh of the fruit as well as in the seeds. The presence of a crystalline substance xylostein, m. p. 124°, in *L. xylosteum* was confirmed; it is probably the poisonous principle of the berry: and isovaleric acid was found in *V. opulus*. The oils from the different species had the following constants: *L. xylosteum*, saponification number (S), 184.85; iodine number (I), 132.8; unsaponifiable (U), 4.9%; oxygen taken up during drying (O), 12%; *L. nigra* (S), 156.53; (I), 101.4; (U), 21.6%; (O), 8.2%; n_D^{23} 1.494; *V. opulus* (S), 192.3; (I), 108.0; (U), 2.3%; (O), 7.1%; n_D^{23} 1.484, d_4^{15} 0.9252; *V. lantana*, (S), 192.5; (I), 121.0; (O), 7.3%; n_D^{23} 1.486; *Sambucus nigra* (S), 190.0; (I), 157.8; (U), 4.5%; (O), 15.1%; n_D^{23} 1.485; d_4^{15} 0.9407; *S. racemosa* (S), 190.8; (I), 162.0; (U), 0.6%; (O), 16.0%; n_D^{23} 1.485; d_4^{15} 0.934; *Symphoricarpus racemosa* (I), 131.8. E. H. R.

The Structure of the Cotton Hair and its Botanical Aspects. HUMPHREY JOHN DENHAM (*Trans. Text. Inst.*, 1922, **13**, 99-112).—A critical and historical review is given of the microscopy and development of the cotton hair, and the facts are discussed in the light of modern theories, especially of the nature of cell-walls in general. It is suggested that as there are so few real botanical abnormalities about cotton, it offers a promising field for the study of cell-walls, including the biochemistry of polysaccharide deposition.

J. C. W.

The Chemical Constituents of Raw Cotton. ROBERT GEORGE FARGHER and JOHN CHARLES WITHERS (*Trans. Text. Inst.*, 1922, **13**, 1-16).—An exhaustive review of the present state

of knowledge of the ash, wax, protein, pigments, and cellulose in raw cotton, with a short account of the behaviour of the minor constituents in technical operations. More than one hundred references to the literature are cited.

J. C. W.

The Chemical Constituents of Green Plants. XVIII. The Acids from the Berry of the Mountain Ash (*Pyrus aucuparia*) which are precipitated by Lead Acetate. HARTWIG FRANZEN and RUDOLF OSTERTAG (*Z. physiol. Chem.*, 1922, 119, 150—165).—On precipitating the acids of the berry of the mountain ash and extracting the fraction with ether, malic acid is mainly obtained. Traces of citric and succinic acids may also be present. Liebig's statement that this berry contains considerable quantities of tartaric and citric acids cannot be confirmed.

S. S. Z.

Tyramine (*p*-Hydroxyphenylethylamine) as the Active Principle of the Drug *Semina cardui Mariæ*. ALFRED ULLMANN (*Biochem. Z.*, 1922, 128, 402—406).—An aqueous extract of the powdered drug was precipitated with phosphotungstic acid and the bases were fractionated by Kossel and Kutscher's process. The final filtrate had a strong pressor action, due to the presence of tyramine which was isolated by extraction with amyl alcohol and identified by its benzoyl derivative and colour reactions.

H. K.

Classification of Soil Moisture. F. W. PARKER (*Soil Sci.*, 1922, 13, 43—54).—It is shown that the dilatometer method (A., 1917, i, 510) does not measure different forms of water in soils and that soils do not contain a considerable quantity of inactive or unfree water. Investigations on the rate of evaporation of water from soils, the vapour pressure at different moisture contents, the equilibrium relations with seeds, and depression of the freezing point due to solid material yielded results which did not indicate the presence of different forms of water in soils. Although the old classification of soil moisture into hygroscopic, capillary, and gravitational water has certain objections it seems to be the best yet offered.

W. P. S.

Relation of the Phosphoric Acid of the Soil to Pot Experiments. G. S. FRAPS (*Texas Agr. Exp. Stat. Bull.*, 1920, 267).—Soils which contain more than the average amount of total nitrogen tend to give higher yields of phosphate to crops than soils containing the same quantities of active phosphate, but the average amounts of total phosphate and nitrogen. Soils containing the same amounts of active phosphate tend to withdraw larger amounts of phosphate when these soils have a higher nitrogen content and a higher total phosphate content. When the soils are arranged in groups according to the amounts of phosphate withdrawn by the crops in the pot experiments, there is a relationship between the amount of phosphate removed from the soil and the active phosphate in the soil, the correlation coefficient for the active phosphate being 0.57, and for total phosphate 0.45. The presence of lime introduces a complication.

CHEMICAL ABSTRACTS.

Organic Chemistry.

Migration of a Double Linking. JOSÉ PUYAL (*Anal. Fis. Quim.*, 1922, 20, 80—83).—*iso*Amyl alcohol (γ -methylbutanol) was dehydrated at 400° , using, as a catalyst, a preparation of infusorial earth. The amino-alcohol prepared from the resulting hydrocarbon by way of the bromohydrin was identical with the base of stovaine, namely, methylethyldimethylaminomethyl carbinol. This alcohol and the corresponding bromohydrin are ordinarily derived from β -methyl- Δ^2 -butylene, $\text{CH}_2\text{:CMe}\cdot\text{CH}_2\text{Me}$. The dehydration of the alcohol used must thus have produced this hydrocarbon and not the expected β -methyl- Δ^3 -butylene. It is supposed that γ -methyl- Δ^2 -butylene, $\text{CHMe}_2\cdot\text{CH}\cdot\text{CH}_2$, is first formed, and that the β -methyl- Δ^2 -butylene results from a rearrangement at the temperature of the reaction by means of a series of alternate hydrations and dehydrations. G. W. R.

Conversion of Allyl Alcohol into Glyceryl Chloro- and Bromo-hydrins. JOHN READ and ERIC HURST (T., 1922, 121, 989—999).

The Action of Acetylene on the Sodium Derivatives of Ketones and the Preparation of Dialkylethynylcarbinols. R. LOCQUIN and SUNG WOUSENG (*Compt. rend.*, 1922, 174, 1427—1429).—When acetylene is passed into a solution of a methyl ketone in an inert solvent containing sodium ethoxide or sodamide, an acetylenic tertiary alcohol is obtained, but with very poor yield (cf. Ruzicka and Fornasir, A., 1919, i, 193). The yield is much improved if the sodium derivative of the ketone is first prepared by means of sodamide and then into this material in ether or benzene the acetylene is passed under pressure. In addition to the required tertiary alcohol, a small amount of a hydrocarbon and some bi-tertiary acetylenic γ -glycol of the type $\text{OR}\cdot\text{CRR}'\cdot\text{C}\equiv\text{C}\cdot\text{CRR}'\cdot\text{OH}$, is obtained. Thus from methyl isohexyl ketone, *methylisohexylethynylcarbinol*, b. p. $83\text{--}85^\circ/10$ mm. and $187\text{--}188^\circ/760$ mm., giving an *allophanate*, m. p. $114\text{--}115^\circ$, is obtained, together with some *methylethylisohexylcarbinol*, b. p. $92\text{--}93^\circ/15$ mm., and its *allophanate*, m. p. $110\text{--}111^\circ$, and the two stereoisomeric forms of a bi-tertiary acetylenic γ -glycol, b. p. $183\text{--}184^\circ/12$ mm., of which the *a*-form has m. p. $66\text{--}68^\circ$, and the *b*-form has m. p. 35° . From methyl nonyl ketone the products are *methylnonylcarbinol*, b. p. $127\text{--}128^\circ/11$ mm., its *allophanate*, *methylethynylcarbinol*, b. p. $131\text{--}134^\circ/14$ mm., and the *a*- and *b*-forms of the γ -glycol, b. p. $237\text{--}238^\circ/10$ mm., and having m. p. $91\text{--}92^\circ$ and $70\text{--}71^\circ$, respectively. Dipropyl ketone yields *dipropylethynylcarbinol*, b. p. $69\text{--}71^\circ/12$ mm., d_4^{20} 0.8691, n_D^{20} 1.4443, and its *allophanate*, m. p. 143° , *dipropylethylcarbinol*, b. p. $78\text{--}79^\circ/16$ mm., and its *allophanate*, m. p. 124° , and the γ -glycol [$\delta\gamma$ -*dipropyl- Δ^2 -decinene-*

$\delta\eta$ -diol], b. p. 174°/18 mm., m. p. 118—119°. Methyl *tert.*-butyl ketone gives *methyltert.butylethylcarbinol*, b. p. 142—144°, d_4^{20} 0.8806, n_D^{20} 1.4441, and its *allophanate*, m. p. 156°, *methyltert.butylethylcarbinol*, b. p. 152°, and its *allophanate*, m. p. 134—135°, and the γ -glycol, b. p. 148—150°/14 mm., of which the α -form has m. p. 88—89° and the β -form m. p. 78°. W. G.

The Unsaturated Reduction Products of Sugars and their Transformations. IV. A Glucoside-like Derivative of a Simple Hydroxyketone, δ -Acetyl-*n*-butyl Alcohol. The Constitution of Fructose. MAX BERGMANN and ARTHUR MIEKLEY (*Ber.*, 1922, 55, [B], 1390—1403).—In a previous communication (this vol., i, 227), it has been shown in the cases of α - and β -methylglucosides and α - and β -methylglucosides that substances of similar constitution may possess very varying degrees of stability and that conclusions with respect to the finer structure of substances which are based on their comparative stability are particularly liable to error. The point appears to be of particular importance for the chemistry of the sugars, and is to be elaborated in a series of papers, of which this is the first.

The relationships of δ -acetyl-*n*-butyl alcohol and its semi-acetal have been investigated. The parent substance is characterised by the extreme readiness with which it reacts with methyl alcohol in the presence of acids, which in concentration even as low as $N/2000$ bring about quantitative acetalisation at the atmospheric temperature in a short time. In this respect, δ -acetyl-*n*-butyl alcohol is more reactive than any aldehydic or ketonic alcohol which has been investigated. As is to be expected, the hydrolysis of the semi-acetal is effected with unusual ease by dilute aqueous acids (the same is true of γ -acetylpropyl alcohol). The observations have considerable interest with reference to the structure of sucrose, in which the 1 : 2-oxide structure has been postulated (cf. Haworth and Law, T., 1916, 109, 1344), as a result of the comparison of sucrose and its hydrolytic products with ethylene oxide and similar unstable systems. The properties of acetylbutyl alcohol semi-acetal show that the ready hydrolysis observed with sucrose is not by any means necessarily dependent on the presence of the ethylene oxide ring, and that further investigation of the structure of the fructose residue is necessary.

δ -Acetyl-*n*-butyl alcohol, $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, or $\text{OH}\cdot\text{COMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, has d_4^{20} 1.0072, n_D^{20} 1.4438. It is transformed by methyl-alcoholic hydrogen chloride into the corresponding *semi-acetal*, $\text{OMe}\cdot\text{COMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, a mobile, very volatile liquid, with a marked odour of camphor, b. p. 76°/99 mm., d_4^{20} 0.94702, d_4^{25} 0.94642, d_4^{30} 0.94445, n_D^{20} 1.4275, n_D^{25} 1.4272, n_D^{30} 1.4264, which can also be prepared in a similar manner from the anhydride of δ -acetyl-*n*-butyl alcohol, $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{COMe}$. The velocity of the former reaction is measured by determining the amount of

unchanged alcohol after given intervals, this being effected by treatment with a known quantity of acetic anhydride dissolved in pyridine, and final estimation of unused acetic acid. The rate of the latter reaction is measured by treating a known amount of the solution of the anhydride in methyl alcoholic hydrogen chloride with an excess of aqueous hydrogen carbonate solution, oxidising the unchanged anhydride with an excess of an ethereal solution of perbenzoic acid, and estimating the excess of the latter by titration of the iodine liberated after addition of potassium iodide.

The velocity of hydrolysis of the *cycloacetal* in water and aqueous hydrochloric acid has also been examined. The method adopted consists in making the experimental solutions alkaline with potassium carbonate after given intervals of time and extracting them thoroughly with ether. After removal of the latter, the residue is acetylated with acetic anhydride in the presence of pyridine. The excess of acid anhydride is destroyed by water, the solution is exactly neutralised by sodium hydroxide, and the amount of acetyl present estimated by hydrolysis.

The $\alpha\delta$ -structure of the oxygen bridge in glucal has been largely adopted on account of its sensitiveness towards acids and the coloration it gives with a pine shaving. Since it is found that these reactions are also shared by γ -acetyl-*n*-butyl alcohol and γ -acetyl-*n*-propyl alcohol, the furoid structure can no longer be regarded as established, and further examination of the ring system of glucal and the related glucosides and polysaccharides is necessary.

H. W.

The Autoxidation of Ethyl Ether. A. M. CLOVER (*J. Amer. Chem. Soc.*, 1922, **44**, 1107—1118).—Ethyl ether absorbs oxygen from the air very slowly at first with the formation of a peroxide by direct addition. The rate of peroxidation becomes much greater in time owing to the catalytic influence of acetaldehyde, which is formed by the spontaneous decomposition of the peroxide. To this peroxide the author assigns the constitution $\text{OEt}\cdot\text{CHMe}\cdot\text{O}\cdot\text{OH}$, which is most in accord with the properties of the compound. The active oxygen content of the pure peroxide is approximately that required for a substance formed by the addition of one molecule of oxygen to one molecule of ether, half the added oxygen being active. The peroxide is formed directly by the action of oxygen on ether. It is volatile and decomposes, especially under the influence of light, with the formation of carbon dioxide, methane, acetaldehyde, and alcohol. With acidified water, it reacts yielding hydrogen peroxide quantitatively. The peroxide is acidic in character. It is shown that hydrogen peroxide is not a primary product of the oxidation of the ether.

W. G.

Action of Dichloroethyl Ether, $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{OEt}$, on the Mixed Magnesium Derivative of Allyl Bromide. R. LESPIEAU (*Bull. Soc. chim.*, 1922, [iv], **31**, 412—414).—By the action of dichloroethyl ether on magnesium allyl bromide in ethereal solution, *c*-chloro- δ -ethoxy- Δ^4 -pentene, $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OEt})\cdot\text{CH}_2\cdot\text{CH}=\text{CH}_2$, b. p. 158—158.5°, d^{20}_4 0.967, n^{20}_D 1.44, is obtained amongst other products,

the yield being small. On bromination it gives α -chloro- δ -dibromo- β -ethoxy-pentane, b. p. 143—144°/16 mm., d^{25}_4 1.630, n^{25}_D 1.5115.

W. G.

Hydrate of Ethylene Oxide. A. MAZZUCHELLI and R. ARMENANTE (*Gazzetta*, 1922, 52, i, 338—346).—Investigation of the freezing-point diagram of the system water-ethylene oxide shows that this oxide forms only one hydrate, $C_2H_4O \cdot 7H_2O$, m. p. $12.8 \pm 0.1^\circ$. The hydrate forms large, transparent, tabular crystals or aggregates of radiating needles, apparently of the triclinic system, and exhibits a marked tendency to give supersaturated aqueous solutions. Its formation is accompanied by considerable contraction and if, as is usually assumed, the molecules of ordinary ice are dimeric and those of ice formed under pressures exceeding 2000 atmospheres monomeric, the water in ethylene oxide hydrate exists as simple molecules.

T. H. P.

Organic Derivatives of Selenic Acid. JULIUS MEYER and WALTER WAGNER (*Ber.*, 1922, 55, [B], 1216—1222).—In continuation of their work on the similarity of selenic and sulphuric acids (cf. Meyer and Wagner, this vol., ii, 372), the behaviour of selenic acid towards organic substances has been examined. Close analogies are again found, but the organic derivatives of selenic acid are distinguished by a much greater liability to internal oxidation, whilst, also, selenic acid appears in some instances to exert a powerful condensing action.

Methyl selenate, Me_2SeO_4 , is prepared as a yellow liquid, d^{25}_4 1.652, n 1.4316, by the action of methyl iodide on silver selenate. It could neither be caused to crystallise nor distilled without decomposition. It deposits selenium at the atmospheric temperature. It is hydrolysed readily by aqueous acids or alkalis. It can be used as a methylating agent in the same manner as methyl sulphate. *Ethyl selenate* is prepared similarly; it has d^{25}_4 1.501, n 1.4445. Propyl selenate could not be obtained by the action of propyl iodide on silver selenate.

Methyl hydrogen selenate is an exceedingly unstable substance the lead and potassium salts of which are described; they decompose very readily. Ethyl hydrogen selenate and its lead, strontium, and potassium salts are too unstable to be analysed. Similar observations are recorded with *n*-propyl hydrogen selenate and its lead, strontium, calcium, and potassium salts.

Potassium phenyl selenate, $KO \cdot SeO_3 \cdot OPh$, colourless leaflets which are moderately stable toward air, is prepared by the action of potassium pyroselenate on a concentrated aqueous solution of potassium phenoxide; it is decomposed by hydrochloric acid into phenol and selenic acid.

The action of selenic acid on phenol is very energetic and proceeds differently from that of sulphuric acid. It was not found possible to isolate a phenolselenonic acid from the products of the change, which appear to consist of complex substances of unknown constitution.

Concentrated selenic acid oxidises aniline with explosive violence;

by mixing the substances in the presence of ether, aniline selenate is obtained as a very unstable, colourless salt. H. W.

The Auto-oxidation of Organic Sulphur Compounds. MARCEL DELÉPINE (*Compt. rend.*, 1922, 174, 1291—1293).—A few further experiments on the auto-oxidation of organic sulphur compounds are described (cf. A., 1910, i, 295, 545, 612; 1911, ii, 1061; 1912, ii, 509) in which it is shown that only a very small amount of the organic vapour is oxidised and the action ceases long before either the oxygen or the organic compound present is used up. It is suggested that these organic sulphur compounds act as their own anti-oxygens (cf. Mourcu and Dufraissac, this vol., i, 250). W. G.

The Chlorinated Dialkyl Sulphides. WILLIAM JACKSON POPE and JAMES LEONARD BRIERLEY SMITH (T., 1922, 121, 1166—1170).

The Sulphilimines, a New Class of Organic Compounds containing Quadrivalent Sulphur. FREDERICK GEORGE MANN and WILLIAM JACKSON POPE (T., 1922, 121, 1052—1055).

Bromination of Acids in the α -Position. CHARLES FREDERICK WARD (T., 1922, 121, 1161—1165).

Studies of the Constitution of Soap Solutions. Sodium Behenate and Sodium Nonoate. ORIEL JOYCE FLECKER and MILLCENT TAYLOR (T., 1922, 121, 1101—1109).

The Effect of High Concentration of Salt on the Viscosity of a Soap Solution. ANNIE MILLCENT KING (*J. Soc. Chem. Ind.*, 1922, 41, 147—148).—The addition of increasing quantities of salt to a solution of sodium palmitate containing 0.5 gram-mol. in 1 kilo. of water was accompanied by a rapid increase in the viscosity, which, however, reached a very decided maximum of 10.5—10.6 C.G.S. units with a concentration of sodium chloride of 0.5N. On further addition of sodium chloride, the viscosity progressively declined to a value of 1.95 at a salt concentration of 0.88N, at which point the liquid commenced to form two heterogeneous layers preliminary to the formation of curd. The progressive addition of potassium chloride to potassium oleate solution caused a similar transition from a clear, mobile liquid to a stiff, transparent jelly, a clear, viscous liquid, and finally two liquid layers and curd separation. It is evident that this behaviour is general for soap solutions. G. F. M.

The Co-ordination Forms of Glycerides. AD. GRÜN (*Oesterr. Chem. Ztg.*, 1922, 25, 73—74; cf. this vol., i, 420).—A further reply to Klimont (this vol., i, 517). H. W.

The Unsaturated Fatty Acids of Egg Lecithin. P. A. LEVENE and IDA P. ROLF (*J. Biol. Chem.*, 1922, 51, 507—513).—In view of the results obtained with liver lecithin (cf. this vol., i, 424), egg lecithin has now been investigated. On hydrolysis,

this yields three unsaturated acids, namely, oleic, linolic, and arachidonic. Egg lecithin differs from liver lecithin in containing only a small proportion of highly unsaturated fatty acids.

E. S.

C₁₈ Fatty Acids. IV. A Rearrangement of the Benzoic Acid Type in the Aliphatic Series. BEN H. NICOLET and ALFRED E. JURIST (*J. Amer. Chem. Soc.*, 1922, **44**, 1136—1141).—When *θ*-diketostearic acid, obtained by the oxidation of *θ*-dihydroxystearic acid with chromic acid, is fused with potassium hydroxide at 160° *θ*-dihydroxystearic acid and α -hydroxy- α -octylsebacic acid are obtained. This is taken as evidence that *θ*-diketostearic acid is an intermediate product in the formation of α -hydroxy- α -octylsebacic acid from *θ*-dihydroxystearic acid by fusion with potassium hydroxide (cf. Le Sueur, T., 1901, 79, 1313). This is probably the first recognised benzoic acid rearrangement of a compound of the type R·CH₂·CO·CO·CH₂·R'. In the fusion of the diketo-acid with potassium hydroxide as described above pelargonic and azelaic acids are also formed by a modified Cannizzaro reaction.

Methyl θ-diketostearate, m. p. 55°, and *ethyl θ-diketostearate*, m. p. 50°, are described.

W. G.

The Esterification of Ethyl Hydrogen Diethylmalonate and of Diethylmalonic Acid. PHILIPPE DUMESNIL (*Bull. Soc. chim.*, 1922, [iv], **31**, 419—420).—In the esterification of ethyl hydrogen diethylmalonate by boiling alcoholic hydrochloric acid, a certain amount of ethyl α -ethylbutyrate is obtained along with the ethyl diethylmalonate. In the esterification of diethylmalonic acid under similar conditions, only a small amount of the ethyl ester is obtained, the main product being ethyl hydrogen diethylmalonate with a trace of ethyl α -ethylbutyrate.

W. G.

The Formation of Malic Acid. JOHN MORRIS WEISS and CHARLES R. DOWNS (*J. Amer. Chem. Soc.*, 1922, **44**, 1118—1125).—A preliminary study of the equilibrium between maleic, fumaric, and malic acids in aqueous solutions over the temperature range 140—200°. At the lower temperature, in aqueous solution, an equilibrium exists among the three acids, but at the higher temperature maleic acid substantially disappears and the equilibrium is between fumaric acid and *i*-malic acid. Further, at the higher temperature approximately the same end-point is reached whether starting with maleic, fumaric, *i*-malic, or *l*-malic acid. Malic acid does not appear to be necessarily an intermediate product in the transformation of maleic acid to fumaric acid. By simple boiling at atmospheric pressure, malic acid solutions are practically unchanged.

For the detection of small amounts of maleic acid in mixtures with fumaric and malic acids, the solution is saturated with respect to fumaric acid at 25°, and then the maleic acid is converted into fumaric acid by the addition of bromine and under the influence of the light from a mercury vapour quartz lamp. The solution

is again brought to 25° and well stirred, and the amount of fumaric acid separating is estimated.

W. G.

The Configuration of the Simple α -Hydroxy-acids. KARL FREUDENBERG and FRITZ BRAUNS (*Ber.*, 1922, **55**, [B], 1339—1352).—It has been shown by Freudenberg (*A.*, 1914, i, 924) that *l*-malic acid is configurationally related to *d*-glyceric and *d*-lactic acids in the grouping $-\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$. Since, further, the relationship of tartaric acid to dextrose has been established, it is only necessary to effect a definite transformation of tartaric acid to malic acid in order to complete the steric series of α -hydroxy-acids. The reduction of *d*-tartaric acid to *d*-malic acid has been effected previously, but the yields are minimal and the conditions are such that a Walden inversion might readily occur. The relationship of the two acids is, however, placed beyond doubt in the following manner.

Methyl *d*-tartrate is converted by a slight excess of acetyl chloride in the presence of methyl acetate into methyl acetyl-*d*-tartrate, m. p. 83—84°, $[\alpha]_D^{25} + 7.40^\circ$ in aqueous solution. The latter is transformed by thionyl chloride in the presence of dry chloroform and anhydrous pyridine into methyl acetyl chloromalonate, $[\alpha]_D^{25} + 3.1^\circ$, which is probably stereochemically not quite uniform by reason of a partial inversion at the halogenated carbon atom. The ester is hydrolysed at the atmospheric temperature by a saturated solution of hydrogen chloride in methyl alcohol (96%) and subsequently by aqueous hydrochloric acid (*d* 1.19), after which the aqueous solution of the acid is allowed to remain in contact with a zinc rod wrapped with a platinum wire until combined chlorine can no longer be detected. After purification through the lead salt, crystalline *d*-malic acid is obtained in 80% yield. It has $[\alpha]_D^{25}$ yellow $+ 2.18^\circ$ in water (8.1%) $- 1.84^\circ$ in water (54.5%), $+ 5.90^\circ$ in acetone and $+ 30.60^\circ$ in pyridine, these values being in close harmony with those of *l*-malic acid quoted in the literature for the sodium *D*-line. The acid is identified further by conversion into the bisphenylhydrazide and amide.

The communication also contains a theoretical discussion of the regularities in steric series, the configuration systems of the simple hydroxy-acids and the monoses, and their mutual relationships, for details of which the original must be consulted.

H. W.

Sativic Acid. ERICH REINGER (*Ber. deut. Pharm. Ges.*, 1922, **32**, 124—131).—The progressive elimination of hydroxyl groups from sativic acid (tetrahydroxystearic acid) prepared by the oxidation of linoleic acid, was carried out by heating the acid with 60% sulphuric acid whereby 1 mol. of water was eliminated, and the unsaturated acid produced was converted by hydrogenation into trihydroxystearic acid. By repeating the operation with this acid, a dihydroxy-unsaturated acid and finally dihydroxystearic acid were obtained, from which a monohydroxy-unsaturated

acid and monohydroxystearic acid were prepared. The constitution of each of the unsaturated acids was determined by an examination of their oxidation products, and that assigned by Eckert (A., 1917, i, 317) to sativic acid, based on the products obtained from it by the action of an oxidising alkali fusion, was confirmed, namely

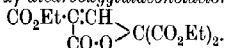
$\text{CH}_3\cdot[\text{CH}_2]_4\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot[\text{CH}_2]_7\cdot\text{CO}_2\text{H}$.
The position of the double bonds in linoleic acid follows accordingly. The preparation and properties of the following substances are described: Trihydroxy-unsaturated acid, $\text{C}_{18}\text{H}_{34}\text{O}_5$, prepared by the elimination of 1 mol. of water from sativic acid, a thick, dark yellow oil of unpleasant odour which is converted by oxidation into the lactone of a trihydroxydecoic acid and by hydrogenation into $\lambda\mu$ -trihydroxystearic acid, a solid, white substance, m. p. 134—135°; from which the dihydroxy-unsaturated acid, $\text{C}_{18}\text{H}_{32}\text{O}_4$, was obtained as a reddish-yellow oil. On oxidation, this substance gave azelaic acid as one of its degradation products, and on hydrogenation it was converted into $\lambda\mu$ -dihydroxystearic acid, identical with that obtained by Hartley from liver and heart fat (*J. Physiol.*, 1909, 38, 353). The further elimination of water from this dihydroxystearic acid was achieved by heating with sulphuric-acetic acid, and the hydrogenation of the product gave the already known λ -hydroxystearic acid, m. p. 80°. G. F. M.

A Property of Ethyl Tartrate. THOMAS STEWART PATTERSON (T., 1922, 121, 1042—1044).

Racemic Acid in Solution. STUART WORTLEY PENNYCUICK (*J. Amer. Chem. Soc.*, 1922, 44, 1133—1136).—The author has measured the interfacial tensions between aqueous solutions of (a) *d*-tartaric acid, (b) *l*-tartaric acid, and (c) racemic acid and the following inert liquids: toluene, paraffin, and a solution of camphor in benzene. The results show that there is no measurable difference in interfacial tension against the several inert liquids between the *d*- and the *l*-acid, but the curve for the racemic acid shows a marked divergence from that of the active acids. These results point to the existence in solution of the racemic acid molecule. As the dilution increases, the curves indicate an increasing dissociation of the racemic acid into the *d*- and *l*-forms. W. G.

Some Transformations of Ethyl γ -Bromo- $\alpha\gamma$ -dicarboxyglutaconate. FRANZ FALTIS and CARLA RUIZ DE ROXAS (*Monatsh.*, 1921, 42, 459—470).—It was hoped that, by removing hydrogen bromide from the γ -bromo- $\alpha\gamma$ -dicarboxyglutaconic ester prepared by Guthzeit and Hartmann (A., 1910, i, 386) it would be possible to obtain ethyl allenetetracarboxylate, $\text{C}(\text{CO}_2\text{Et})_2\cdot\text{C}\cdot\text{C}(\text{CO}_2\text{Et})_2$. This hope was not realised, but a number of new products were obtained. The bromo-compound was prepared by brominating the copper salt of ethyl dicarboxyglutaconate in chloroform solution. The bromodicarboxyglutaconic ester decomposes slowly when heated on the water-bath. Attempts to remove hydrogen bromide by heating the compound with diethyl-

aniline (method of Crossley and Le Sueur) were unsuccessful. When distilled in a vacuum, bromodicarboxyglutaconic ester decomposed into ethyl bromide and a lactonic compound which was proved to be triethyl γ -hydroxy- α - γ -dicarboxyglutaconolactone,



It distils at 212–216°/16 mm. as a green, fluorescent oil, crystallising in star-shaped crystals, m. p. 28–30°. In its intense fluorescence it resembles the structurally similar methylaminocitraconic methylimide and ethyl aminocyanofurancarboxylate, the only other known fluorescent aliphatic compounds. When the lactone is treated with alcoholic potassium hydroxide or potassium ethoxide, the lactone ring is not ruptured, but a carbethoxyl group is split off with a molecule of carbon dioxide and the enol potassium salt of diethyl γ -hydroxy- α -carboxyglutaconolactone, $\text{CO} \cdot \text{C}(\text{CO}_2\text{Et}) > \text{CH}$, is obtained. It forms a copper salt, lustrous, orange needles, losing water of crystallisation at 105°, m. p. 195° (decomp.). When ethyl bromodicarboxyglutaconate is treated with potassium ethoxide, it appears to behave in a similar manner to the above lactonic ester, losing a carbethoxy-group and carbon dioxide and leaving a product which gives an intense bluish-violet coloration with ferric chloride, and forms a green copper salt containing bromine.

E. H. R.

Steric Transformations with α -Sulphonedialiphatic Acids. R. AHLBERG (*Ber.*, 1922, 55, [B], 1279–1281).—A preliminary communication due to the recent publication by Fitger (this vol., i, 107, 108).

The same α -sulphonedibutyric acid, $\text{SO}_2(\text{CHEt} \cdot \text{CO}_2\text{H})_2$, m. p. 132°, is obtained by the oxidation of *meso*-, *r*-, or optically active α -thiodibutyric acids with potassium permanganate. The experiments with *l*- α -thiodibutyric acid, however, prove that a certain amount of optically active α -sulphonedibutyric acid exists in the freshly oxidised solution which becomes inactive in the course of a few hours. Preliminary experiments show that the α -sulphonedibutyric acid, m. p. 152° (which is thus proved to be the racemic form), can be resolved into its optical components by brucine in aqueous solution; the *l*-acid undergoes auto-racemisation when dissolved in water, the undissociated acid being affected more slowly than its ions.

Similar results are obtained with α -sulphonediisovaleric acid, which, however, is rather more stable optically than its lower homologue.

H. W.

Preparation of Formaldehyde or its Polymerides from Mixtures of Carbon Monoxide and Hydrogen. ERNEST JOSEPH LUSH (*Brit. Pat.* 180016).—When mixtures of carbon monoxide and hydrogen in suitable proportions such as may be obtained by the purification of "suction gas" or water gas, are passed rapidly over catalysts prepared, preferably, from a mixture

z*

of 4 parts of nickel, 1 part of copper, and 5 parts of alumina, large quantities of formaldehyde or its polymerisation products are formed, and the residual gas consists mainly of methane and hydrogen. The gas is preferably forced through the catalyst at an initial temperature of 300–400°, under 10 atmos. pressure, at such a velocity as to ensure that the temperature does not fall below 160–180° on leaving the catalyst. To promote rapid cooling thereafter, the high-pressure gas is allowed to issue from a small constriction and is then led into water scrubbers to remove the formaldehyde. In order to restore the activity of the catalyst, steam is blown through periodically, or, alternatively, it may be mixed with the compressed gases. G. F. M.

Conversion of Active Glyceraldehyde into Active Glyceric Acid. A. WOHL and R. SCHEULENBERG (*Ber.*, 1922, 55, [D], 1404–1408).—*d*-Glyceraldehydedimethylacetal, $[\alpha]_D^{25} + 21.2^\circ$ in aqueous solution, is hydrolysed by aqueous *N*/10-sulphuric acid and the solution is oxidised with yellow precipitated mercuric oxide in the presence of barium hydroxide. A dextrorotatory barium glycerate, having $[\alpha]_D^{25} + 8.45^\circ$ in aqueous solution is thereby obtained. Since the active glyceric acids rotate in the opposite sense to their salts it follows that *d*-glyceraldehyde is genetically related to *l*-glyceric acid. H. W.

Bisulphite Compounds of Oximinoketones and Glyoximes. C. GASTALDI and G. BRAUNIZER (*Gazzetta*, 1922, 52, i, 307–316).—The action of sodium hydrogen sulphite on chloroximinoacetone yields: (1) a compound, $C_3H_5O_5NCISNa$, which loses the SO_3Na group quantitatively as sulphurous acid when heated with dilute hydrochloric acid. This behaviour is that of bisulphite compounds having the SO_3Na group united to a carbon atom, so that the formula of the above compound is probably $SO_3Na \cdot O \cdot CMe(OH) \cdot CClNOH$; (2) a compound which results from further action of the sodium hydrogen sulphite and subsequent decomposition, crystallises in cubes, and is free from nitrogen and chlorine. This compound has not been obtained pure, but when treated with phenylhydrazine in dilute acetic acid, it yields a compound, $C_9H_9O_2N_3$, which is reduced by sodium amalgam to phenylhydrazineacetic acid, ammonia, and aniline, and hence appears to be 2-phenyl-1:3-dihydro-1:2:3-triazole-4-carboxylic acid; under similar conditions, 2-phenyl-1:2:3-triazole-4-carboxylic acid (cf. Pechmann, A., 1891, 1112) yields phenylhydrazineacetic and hydrocyanic acids.

Thus, the action of sodium hydrogen sulphite on oximinoketones (cf. A., 1921, i, 602) is exerted principally on the group $\cdot C \cdot NOH$, transforming this into the group $SO_3Na \cdot \dot{C} \cdot NH \cdot OH$, and hence yielding a derivative of hydroxylamine. In a further stage of the action, another molecule of sodium hydrogen sulphite reacts, with formation of compounds derivable from either ammonia or aminosulphonic acid,

$SO_3Na \cdot \dot{C} \cdot NH \cdot OH + NaHSO_3 \rightarrow SO_3Na \cdot \dot{C} \cdot NH \cdot SO_3Na + H_2O$.
An analogous reaction occurs with carbonyl compounds and with

certain unsaturated compounds having a double linking between two carbon atoms. It may be that the same reaction applies to compounds with a double linking between oxygen and nitrogen and that the interaction of nitrous acid and sodium hydrogen sulphite may be explained by assuming that the $\cdot\text{N}=\text{O}$ group of the acid behaves similarly to the $\text{:C}=\text{O}$ of carbonyl compounds, the $\text{:C}=\text{N}\cdot$ of oximinoketones, and the $\text{:C}=\text{C}\cdot$ of some unsaturated compounds, so that the initial product is hydroxylaminohydroxysulphonic acid, $\text{SO}_3\text{Na}\cdot\text{N}(\text{OH})_2$; from the latter, by further action of one or two molecules of sodium hydrogen sulphite, hydroxylamine-disulphonic and the so-called nitrilosulphonic acids would result. An analogous interpretation may be given to the formation of the compound $\text{K}_2\text{SO}_3\cdot 2\text{NO}$, to which Raschig ascribes the structure $\text{KO}\cdot\text{N}(\text{NO})\cdot\text{SO}_3\text{K}$.

The compound $\text{SO}_3\text{Na}\cdot\text{O}\cdot\text{CMe}(\text{OH})\cdot\text{CCl}\cdot\text{NOH}$ forms small, colourless rhombohedra and decomposes when either dissolved in water or exposed to the air.

The acid $\text{C}_6\text{H}_5\text{O}_2\text{N}_3$ (see above) is obtained in colourless needles containing benzene of crystallisation, and when freed from benzene has m. p. $178-179^\circ$ (evolution of carbon dioxide).

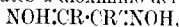
The analogous acid, $\text{C}_6\text{H}_5\text{O}_2\text{N}_3\text{Br}$, obtained when *p*-bromophenylhydrazine is used in place of phenylhydrazine, forms pale yellow, lustrous laminæ, m. p. 185° (evolution of carbon dioxide).

The compound $\text{SO}_3\text{Na}\cdot\text{O}\cdot\text{CMe}(\text{CH}\cdot\text{NOH})\cdot\text{NH}\cdot\text{SO}_3\text{Na}$, and the corresponding potassium compound, obtained when methylglyoxime is treated with sodium (potassium) hydrogen sulphite solution saturated with sulphur dioxide, form colourless needles containing water of crystallisation, give yellow solutions in dilute alkali hydroxide solutions, and do not yield insoluble compounds with nickel salts. When treated with phenylhydrazine, they give methylglyoxal phenylosazone, and when heated with 10% sulphuric acid solution, small proportions of oximinoacetone.

When the sodium hydrogen sulphite compounds of oximino-ketones and of methylglyoxime are hydrolysed by means of 10% hydrochloric acid, the SO_3Na group united to carbon is eliminated as sulphurous acid, and that united to nitrogen as sulphuric acid. Since these reactions are almost quantitative, the proportions of the SO_3Na group combined in the two ways may be estimated.

T. H. P.

Dioximes. II. G. PONZIO and G. RUGGERI (*Gazzetta*, 1922, 52, i, 289-301; cf. this vol., i, 17).—If, in accordance with the Hantzsch-Werner hypothesis, the isomerism of the α -dioximes is attributed to the different relative positions occupied in space by the two hydroxyl groups, the properties of methylacetylgl oxime (dimethyltriketone α -dioxime) not only indicate no choice between the four possible configurations, but fail also to explain the behaviour of this compound towards nitrogen tetroxide. Indeed, whereas the latter dehydrogenates α -dioximino-derivatives,



giving the corresponding peroxides (furoxans), $\text{R}\cdot\text{C}_2\text{N}_2\text{O}_2\cdot\text{R}'$, it

$\text{2}\cdot\text{2}$

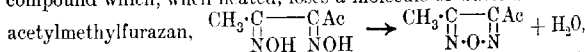
converts methylacetylgyoxime into a keto- ψ -nitroleoxime, namely, α -oximino- β - ψ -nitrole- γ -ketopentane, $\text{NOH}\cdot\text{CMe}\cdot\text{CAc}\cdot\text{N}_2\text{O}_3$. Hence the two oximino-groups of methylacetylgyoxime are not equivalent and as a similar phenomenon is encountered with other α -dioximes, but only for one form of them, there can be no question in this case of geometrical isomerism.

Three configurations are possible for α -oximino- β - ψ -nitrole- γ -ketopentane according as the structure of the N_2O_3 group is represented by $\text{C}(\text{NO})\cdot\text{NO}_2$, $\text{C}\cdot\text{N}\cdot\text{O}\cdot\text{NO}_2$, or $\text{C}\cdot\text{NO}\cdot\text{NO}_2$. When this compound is treated with aqueous ammonia, it gives rise to methylaminoglyoxime, which is probably formed as the result of the following reactions: (1) The hydrolysis, $\text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{C}(\text{NO})(\text{NO}_2)\cdot\text{CO}\cdot\text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}(\text{NO})\cdot\text{NO}_2 + \text{CH}_3\cdot\text{CO}_2\text{H}$; (2) the isomerisation, $\rightarrow \text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{C}(\text{NO}_2)\cdot\text{N}\cdot\text{OH}$, and (3) substitution of the nitro-group of the methylnitroglyoxime by the amino-group, $\text{NOH}\cdot\text{CMe}\cdot\text{C}(\text{NO}_2)\cdot\text{NOH} + \text{NH}_3 \rightarrow \text{NOH}\cdot\text{CMe}\cdot\text{C}(\text{NH}_2)\cdot\text{NOH} + \text{HNO}_2$. The first of these reactions has been already observed with the amylketo- ψ -nitrole, $\text{N}_2\text{O}_3\cdot\text{CEtAc}$, which yields propylnitrole and acetic acids when treated with potassium hydroxide solution (Ponzio, A., 1899, i, 667). The third stage, replacement of a nitro- by an amino-group by the action of ammonia, is very common with aromatic polynitro-derivatives, and is met also in the conversion of phenylnitroformaldehyde arylhydrazones into the corresponding hydrazidines,

$\text{NO}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{NHAr} + \text{NH}_3 \rightarrow \text{NH}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{NHAr} + \text{HNO}_2$
(Ponzio, A., 1910, i, 443, 699). Further, the compound obtained when α -oximino- β - ψ -nitrole- γ -ketopentane is treated with ammonia is identical with the one formed by replacement of the chlorine atom of chloromethylglyoxime by the amino-group,

$\text{NOH}\cdot\text{CMe}\cdot\text{CCl}\cdot\text{NOH} + \text{NH}_3 \rightarrow \text{NOH}\cdot\text{CMe}\cdot\text{C}(\text{NH}_2)\cdot\text{NOH}$,
and is undoubtedly methylaminoglyoxime, which is both an α -dioxime and a primary amine.

Acetylmethylglyoxime forms a diacetyl derivative, an internal anhydride, and a trioxime, and may be regarded as an equilibrated mixture of the tautomeric nitroso-oxime, $\text{NOH}\cdot\text{CMe}\cdot\text{CHAc}\cdot\text{NO}$, and α -dioxime, $\text{NOH}\cdot\text{CMe}\cdot\text{CAc}\cdot\text{NOH}$. The first of these formulæ indicates how the action of nitrogen peroxide may yield α -oximino- β -nitroso- β -nitro- γ -ketopentane, whilst the second explains (1) the acetylation by the action of acetic anhydride in the cold to a compound which, when heated, loses a molecule of water and forms acetylmethylfurazan,

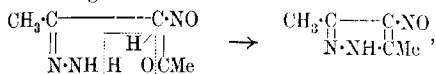


and (2) the formation, by the action of hydroxylamine, of dimethyl-triketone-trioxime, $\text{NOH}\cdot\text{CMe}\cdot\text{C}(\text{NOH})\cdot\text{CMe}\cdot\text{NOH}$, in which, as will be shown later, three oximino-groups undoubtedly exist. Thus, it must be assumed that the hydrogen atom of the β -oximino-group is mobile and may migrate from the oxygen to the carbon with consequent isomerisation of the group $\text{NOH}\cdot\text{C}\cdot\text{C}\cdot\text{NOH}$ into $\text{NOH}\cdot\text{C}\cdot\text{CH}\cdot\text{NO}$.

The β -oximic group of acetylmethylglyoxime is the one which

pre-exists in oximinoacetylacetone (dimethyltriketone β -monoxime), from which the dioxime is formed by the action of hydroxylamine. If it is assumed that the oximic hydrogen of oximinoacetylacetone also is mobile and may migrate from the oxygen to the carbon, $\text{NOH}\cdot\text{C}\cdot\text{Ac}_2 \rightleftharpoons \text{NO}\cdot\text{CH}\cdot\text{Ac}_2$, it is possible easily to explain its conversion into derivatives of 4-nitrosopyrazole, $\text{N} \begin{smallmatrix} \text{CH}\cdot\text{C}\cdot\text{NO} \\ \text{NH}\cdot\text{CH} \end{smallmatrix}$, by

treatment with hydrazine, phenylhydrazine, semicarbazide, etc. (cf. Wolff, Bock, Lorentz, and Trappe, A., 1903, i, 210; Sachs and Alsleben, A., 1907, i, 356). Thus, if oximinoacetylacetone behaves as $\alpha\gamma$ -diketo- β -nitrosopentane, the action of hydrazine should yield the hydrazone, the latter then losing the elements of water according to the scheme:



giving 4-nitroso-3:5-dimethylpyrazole.

Acetylmethylglyoxime, best prepared by treating oximinoacetylacetone in the cold with the theoretical proportion of hydroxylamine hydrochloride and with sodium acetate in highly concentrated aqueous solution, forms elongated laminae, often rectangular and sometimes united in pennate aggregates, m. p. 141° (decomp.), and dissolves in concentrated sulphuric acid with an emerald-green coloration and in sodium hydroxide solution without coloration. The low melting point, 128° , given by Wolff is due to the fact that the compound undergoes alteration when heated with water or with an organic solvent containing water. In aqueous solution, it does not attack nickel, cobalt, copper, or iron, or react with salts of these metals. Its *diacetyl* derivative, $\text{C}_8\text{H}_{12}\text{O}_5\text{N}_2$, forms white prisms, m. p. $77\text{--}78^\circ$, and yields methylacetylfulurazan when heated with water.

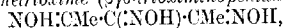
α -Oximino- β - ψ -nitrole- γ -ketopentane, $\text{C}_5\text{H}_7\text{O}_5\text{N}_3$, crystallises in white prisms, m. p. $102\text{--}103^\circ$ (decomp.), and dissolves without coloration in cold concentrated sulphuric acid, giving a solution from which it is precipitated on addition of water. It is stable in the air, but decomposes rapidly, with evolution of nitrous fumes, when kept in a closed vessel. Even weak bases hydrolyse it with rupture of the carbon atom chain between the ψ -nitrole and carbonyl groups; the first products are acetic acid and methyl-nitroglyoxime, these then undergoing further changes, the nature of which varies with the base used. When treated in aqueous suspension with silver carbonate, it yields carbon dioxide and silver nitrite.

Aminomethylglyoxime, $\text{NOH}\cdot\text{CMe}\cdot\text{C}(\text{NH}_2)\cdot\text{NOH}$, prepared by treating the preceding compound with aqueous ammonia and purified by precipitation of its nickel derivative and removal of the nickel from the latter as potassium nickelocyanide, forms white needles or laminae, m. p. $183\text{--}184^\circ$ (partial sublimation), and in aqueous solution attacks nickel, cobalt, iron, and copper, slowly at the ordinary temperature and rapidly at about 100° .

The *nickel* salt, $(C_3H_6O_3N_3)_2Ni.H_2O$, forms orange-red laminae and becomes anhydrous at 130° . The *dibenzoyl* derivative, $C_{16}H_{15}O_4N_3$, crystallises in white needles, m. p. 206° . The *hydrochloride*, $C_3H_7O_3N_3.HCl$, forms white prisms, m. p. 170° (evolution of gas).

Acetylmethylfurazan, $C_5H_6O_3N_2$, forms a colourless liquid with a suffocating odour, heavier than water, b. p. $154.5^\circ/742.8$ mm., and yields methylfurazancarboxylic acid when oxidised with permanganate. The *oxime*, $C_5H_7O_3N_3$, crystallises in white laminae, m. p. 86° , and forms an *acetyl* derivative, $C_5H_6ON_2.NOAc$, crystallising in long, white needles, m. p. $60-61^\circ$, and a *benzoyl* derivative, $C_{12}H_{11}O_3N_3$, crystallising in white prisms, m. p. $120-121^\circ$. The *hydrazone*, $C_5H_6ON_2.N.NH_2$, forms white prisms, m. p. 120° , with previous softening, the *phenylhydrazone*, $C_{11}H_{12}ON_4$, straw-coloured needles, m. p. 117° , and the *semicarbazone*, $C_6H_9O_2N_5$, white prisms, m. p. 232° .

Dimethyltriketetonetrixime ($\beta\gamma\delta$ -trioximinopentane),



the first compound of its class, purified by means of its nickel compound, forms white prisms, m. p. 175° (decomp.), dissolves in concentrated sulphuric acid and in alkali hydroxide solutions without coloration, and in aqueous solution readily attacks compact nickel, cobalt, copper, and iron. Under the action of acetic anhydride and fused sodium acetate, the β -oximino-group undergoes acetylation, whilst the other two oximino-groups unite with loss of water, the resulting compound being the acetyl derivative of methylacetylfurazanoxime, $\begin{matrix} N.CMe \\ | \\ O-N \end{matrix} > C.CMe.NOAc$. The *nickel* salt,

$(C_5H_8O_3N_3)_2Ni$, crystallising in orange-red prisms or needles, turns brown without melting at about 260° , and dissolves in alkali hydroxide or ammonia solution, giving an orange-red solution; it is of the type of compounds considered by Tschugaev (A., 1905, i, 743; 1908, i, 554; T., 1914, 105, 2187) as characteristic of the so-called syn-forms of the α -dioximes, being derived from two molecules of the trioxime by replacement of two atoms of oximino hydrogen by an atom of nickel. Other $\alpha\beta\gamma$ -trioximes yield analogous nickel derivatives. The *tribenzoyl* compound, $C_{26}H_{21}O_6N_3$, forms white prisms, m. p. $191-192^\circ$.
T. H. P.

Croconic Acid and Leuconic Acid. B. HOMOLKA (Ber., 1922, 55, [B], 1310-1311).—Leuconic acid is hydrolysed by cold, aqueous sodium carbonate solution to glyoxal and sodium mesoxalate, whereby its constitution, $\begin{matrix} CO.CO \\ | \\ CO.CO \end{matrix} > CO$, is established. The position of the two hydroxyl groups in croconic acid remains undecided.
H. W.

The Preparation of Pure Galactose. G. MOUGNE (Bull. Soc. Chim. Biol., 1922, 4, 206-208).—When prepared by Clark's method (A., 1921, i, 647), galactose is probably contaminated with dextrose. In the method described, dextrose is removed from the mixed monosaccharoses obtained by the hydrolysis of lactose

by fermentation with top yeast. The galactose, which is unattacked, is recrystallised from 75% alcohol. E. S.

The Action of Ammonia and of Amino-compounds on Reducing Sugars. I. The Action of Ammonia on Dextrose and Lævulose. ARTHUR R. LING and DESSHAW RATTONJI NANJI (*J. Soc. Chem. Ind.*, 1922, **41**, 151—155r).—Dextrose unites with ammonia at 35° to form an additive compound, *glucose-ammonia*, $C_6H_{12}O_5 \cdot NH_3$, probably $OH \cdot CH_2 \cdot [CH(OH)]_4 \cdot CH(OH) \cdot NH_2$, analogous to aldehyde-ammonia, which can be isolated as a pale amber-coloured, friable mass by evaporating the solution in a vacuum at a temperature not exceeding 37—38°. It is extremely hygroscopic, and even in the solid state gives off ammonia. It reduces alkaline copper and silver solutions in the cold with the formation of a mirror. In solution, it is dissociated, for the specific rotatory power is the same as that of the sugar freed from ammonia. An aqueous solution of the sugar was obtained from glucose-ammonia by aspirating air through it. The sugar could not be crystallised, but it reduced potassium permanganate in the cold, which has been shown to be a property of the so-called γ -glucose. Its specific rotatory power $[\alpha]_D^{20} +4.4^\circ$, and it was shown to be a mixture of aldose and ketose in equilibrium, the point of equilibrium being changed according to the reaction of the solution, and in $N/4$ hydrochloric acid 100% aldose is present. Lævulose when treated with ammonia is partly converted into aldose and this unites with ammonia, the solution behaving in every way similarly to the product from dextrose. When the ammonia is removed from the solution a similar mixture of aldoses and ketoses in equilibrium is obtained. G. F. M.

Preparation of Complex Iron Compounds of the Phosphoric Esters of Higher Aliphatic Polyhydroxyl Compounds. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 338735; from *Chem. Zentr.*, 1921, iv, 1223).—Phosphoric esters of polyhydroxyl compounds are treated with iron compounds in the presence of alkalis. The calcium salt of lævulose diphosphoric acid by reaction with oxalic acid, sodium hydroxide, and ferric chloride gives the *normal iron salt* of the ester, a white powder insoluble in water. By the action of 33% sodium hydroxide solution on the normal salt, a deep reddish-brown solution is obtained, from which, after the addition of 95% ethyl alcohol, the complex *iron salt* separates as a dark brown oil which may be obtained as a dark brown powder by agitation with absolute alcohol. It contains phosphorus 6.26%, sodium 11.48%, and iron 15.12%. The complex *iron salt* of lævulose-monophosphoric acid is a brown powder containing phosphorus 5.27%, sodium 9.87%, and iron 14.11%. The complex *iron salt* of sucrose monophosphoric acid contains phosphorus 4.89%, sodium 4.01%, and iron 12.21%. The complex *iron salt* of mannitol monophosphoric acid contains phosphorus 3.82%, sodium 11.40%, and iron 20.83%. The compounds are slightly soluble in water with alkaline reaction. Phosphorus is in organic combination. The products have therapeutic uses. G. W. R.

Chemistry of Starch. V. Methyl and Acetyl Products of the "Polyamyloses." HANS PRINGSHEIM and WALTER PERSCH (*Ber.*, 1922, **55**, [B], 1425—1433).—The conversion of tetra-amylose into octamethyltetra-amylose has been described previously (Pringsheim and Persch, this vol., i, 113); the third hydroxyl group could not, however, be methylated, and it was therefore suggested tentatively that it was concerned in the union of the diamylose complexes in tetra-amylose. This does not appear to be the case, since octamethyltetra-amylose is converted readily by acetic anhydride and pyridine into the corresponding *tetra-acetate*, $(C_6H_7O_2Mc_2Ac)_4$, hexagonal rods which darken without melting at 120° , $[\alpha]_D^{20} + 118.62^\circ$ in ethyl alcohol. Diamylose resembles tetra-amylose in that it is converted by successive treatment with methyl sulphate and sodium hydroxide and methyl iodide and silver oxide into *tetramethyldiamylose*, hexagonal plates which do not melt below 200° , $[\alpha]_D^{20} + 143.74^\circ$ in ethyl alcoholic solution. Attempts to methylate the third hydroxyl group were unsuccessful.

The behaviour of the polyamyloses of the β -series towards methylation is peculiar. With hexa-amylose, reducing action towards Fehling's solution is observed after a single treatment with methyl sulphate and sodium hydroxide, although the solution was not at any time acidic. With triamylose, the phenomenon was first noticeable after the first methylation with silver oxide and methyl iodide and became more marked after a second treatment with the same reagents.

The author's method of acetylation with acetic anhydride and pyridine permits without depolymerisation the conversion of the slimes obtained by the degradation of starch with *Bacillus macerans*, into *hexa-amylose dodeca-acetate*, aggregates of minute needles, which shrinks at 135° , but does not melt definitely below 215° , $[\alpha]_D^{20} + 95.77^\circ$, $[\alpha]_D^{25} + 95.77^\circ$, when dissolved in glacial acetic acid. It is converted by alcoholic potassium hydroxide solution into the initial material, which is thus characterised as α -hexa-amylose.

H. W.

Chemistry of Starch. VI. Polyamyloses. HANS PRINGSHEIM and DIAMANDI DERNIKOS (*Ber.*, 1922, **55**, [B], 1433—1445).—The acetylation of polyamyloses with acetic anhydride and pyridine has been extended to α -tetra-amylose, which, as expected, yields α -tetra-amylose dodeca-acetate, $[C_6H_7O_2(OAc)_2]_4$, needles, $[\alpha]_D^{20} + 115.8^\circ$ in glacial acetic acid solution, the molecular weight of which has been determined in benzene and bromoform. It is reconverted by alcoholic potassium hydroxide solution into α -tetra-amylose, the identity of which is established by the determination of its molecular weight. The application of this method of acetylation to polyamyloses of the β -series has led to surprising results, since β -hexa-amylose is thereby converted into the same triamylose nona-acetate, $[C_6H_7O_2(OAc)_3]_3$, $[\alpha]_D^{20} + 117.9^\circ$ in glacial acetic acid solution, as was obtained previously by acetylation in the presence of zinc chloride; a possible explanation of the unexpected depolymerisation is found in the fact that the experi-

mental conditions, by reason of the sparing solubility of the initial material, were necessarily more drastic than those adopted with the members of the α -series.

Karrer has recently expressed the opinion that β -hexa-amylose is not depolymerised by acetylation in the presence of zinc chloride, in which case Pringsheim's triamylose must be merely de-acetylated β -hexa-amylose (this vol., i, 435). Karrer's arguments are criticised in detail. Reasons are advanced for considering that data obtained from the action of acetyl bromide on polysaccharides are completely unsatisfactory in the quantitative form given to them by Karrer. The compounds of triamylose with the alkali hydroxides have, according to Karrer, the formula $C_{12}H_{20}O_{10} \cdot NaOH$. It is pointed out that a compound prepared in accordance with Karrer's directions by the precipitation of a solution of β -hexa-amylose in aqueous sodium hydroxide (10%) with alcohol had the composition, $(C_6H_{10}O_5)_3 \cdot NaOH$, but great value cannot be placed on the results of analyses of these substances, since their alkali content is greatly dependent on the experimental conditions. Hydrolysis of triamylose acetate with sodium ethoxide followed by thorough washing of the precipitate with absolute alcohol gives a substance, $(C_6H_{10}O_5)_3 \cdot NaOH$. Contrary to Karrer's observations, β -hexa-amylose invariably contains a higher percentage of water of crystallisation than triamylose. The solubilities of the two substances in water are not identical; as concordant result of two different methods, the solubility of triamylose in water at 20° is 1.3 by weight and 1.34% by volume, the corresponding figures for β -hexa-amylose being 2.4 and 2.65. Contrary to Karrer, the optical activity of triamylose is lower than that of β -hexa-amylose. A revision of the crystalline forms of triamylose and β -hexa-amylose confirms Karrer's observation of their identity. Attempts to determine the molecular weight of triamylose in boiling water were unsuccessful, since a true solution could not be obtained.

Measurements of the crystals of diamylose, triamylose, and β -hexa-amylose, tetra-amylose, and α -hexa-amylose are recorded.

H. W.

Chemistry of Starch. VII. Relationship of the α - and β -Polyamyloses to the Content and Integument Substance of the Starch Granule. HANS PRINGSHEIM and KURT GOLDSTEIN (*Ber.*, 1922, 55, [B], 1446—1449).—It has been shown by Samec and his co-workers that starch can be separated by electrodialysis of its solutions into erythroamyloses and amyloamyloses. The close relationship of these substances to the β - and α -amyloses is illustrated.

The erythroamyloses give a brown and the amyloamyloses a blue coloration with starch; the iodine additive compounds with β -polyamyloses are brownish-red whereas those with α -polyamyloses are green when dry, but become blue when moistened. The erythroamyloses and amyloamyloses have $[\alpha]_D +195$ to 196° and $+189^\circ$, respectively; the β -polyamyloses are more highly

active than the α -compounds, the respective specific rotations being $+152^\circ$ to 158° and $+132^\circ$ to 136° , respectively. The molecular weights of the erythroamyloses and amyloamyloses are approximately 130,000—140,000 and 80,000; the ratio is approximately 3:2, which is the same as for the fundamental tri- and di-amyloses of the β - and α -polyamyloses. Fermentation of the amylopectins and amyloses by *Bacillus macerans* shows that β -polyamyloses are obtained in larger yield from the erythro-, α -poly-amyloses from the amyloamyloses. Iodine unites more readily with amyloamyloses than with erythroamyloses; similarly, the fractional addition of iodine to a solution containing α -tetra-amylose and β -hexa-amylose results in the initial precipitation of green needles of the α -tetra-amylose compound, followed by brownish-red prisms of tri-iodo-hexa-amylose, the yields and separation being highly satisfactory.

The optical activity of glycogen and its behaviour towards *B. macerans* allies it closely to the electrolyte-free amylopectins; an exact determination of its molecular weight (which has been found by methods of little trustworthiness to be 140,000) is, however, necessary before it can be regarded definitely as an erythro-amylose.

H. W.

Constitution of Polysaccharides. IV. Inulin. JAMES COLQUHOUN IRVINE, ETTIE STEWART STEELE, and MARY ISOBEL SHANNON (T., 1922, **121**, 1060—1078).

Inulin. II. Inulin and Glycogen. HANS PRINGSHEIM and MAX LASSMANN (*Ber.*, 1922, **55**, [B], 1409—1414).—Redeterminations of the molecular weight of inulin acetate dissolved in glacial acetic acid by the method of Barger as modified by Rast have confirmed the previous measurements, but the process cannot be applied in the cases of the acetates of glycogen and soluble starch. The method does not appear to be practicable for the determination of molecular weights exceeding 3000.

Glycogen is transformed by acetic anhydride in the presence of pyridine into *glycogen acetate*, $C_{12}H_{16}O_8$, m. p. 165° (indefinite), $[\alpha]_D^{25} +159.6^\circ$ when dissolved in pyridine; when hydrolysed by alcoholic potassium hydroxide, it gives a white, pulverulent glycogen, which is coloured brownish-red by iodine and is hydrolysed in the same manner as the initial glycogen by "fermasol D.S." (a preparation containing diastase).

Starch which had been rendered soluble by being heated at 190° in the presence of glycerol and did not reduce Fehling's solution was converted into its acetate. The product differs from glycogen acetate, whereas the same substance is prepared by the methylation of soluble starch or glycogen (Karrer, this vol. i, 11).

The differing behaviour of starch and glycogen towards iodine has been ascribed by Karrer (*loc. cit.*) to the presence of impurities. This is regarded as improbable since the de-acetylated starch and glycogen acetates retain their characteristic properties towards iodine.

H. W.

Inulin. III. HANS PRINGSHEIM and ALEXANDER ARONOWSKY (*Ber.*, 1922, 55, [B], 1414—1425).—Inulin, in the solid condition and in its colloidal solution, is a product of the association of a trebly polymerised anhydro-trifructose. In the latter, the fructose residues are not present in the same form as in fructose stable in solution [with butylene oxide oxygen bridge], but exist as the so-called γ -fructose which probably contains an ethylene oxide ring. The ready hydrolysis of inulin, and particularly of tri-fructose, thereby receives an explanation.

In previous communications (Pringsheim and Aronowsky, A., 1921, i, 545; Pringsheim and Lassmann, preceding abstract), it has been shown that inulin triacetate is fundamentally composed of nine fructose residues. The proof of the identity of the inulin regenerated from the acetate with the original inulin was obtained from Röntgen spectrographic observations. Attempts to confirm this identity by fermentative hydrolysis with *Penicillium glaucum* have led to interesting results since the properties of the ferment are found to depend largely on the conditions of its culture. From the same specimen of *Penicillium* three cultures are obtained, the first of which, nourished with sucrose, does not hydrolyse inulin, whereas the second, nourished with natural inulin, hydrolyses the latter, but not de-acetylated inulin acetate, whilst the third, nourished with artificial inulin, hydrolyses both inulins. It is not considered that these observations afford a proof of the different degrees of polymerisation in the two products.

Previous attempts to hydrolyse inulin with ferments or acids have never led to the isolation of a di- or tri-saccharide, and renewed efforts in this direction are now recorded. The action of phenylhydrazine acetate on an aqueous solution of inulin leads mainly to the production of glucosazone, but indications are also obtained that a second osazone which is soluble in hot water is formed; it could not, however, be isolated in quantity sufficient for further experiment.

The acetolytic degradation of inulin cannot be effected with acetic anhydride and sulphuric acid, since the products are too readily carbonised. A suitable acetylating mixture is secured by using glacial acetic acid (2 parts) and acetic anhydride (1 part) for each part of inulin; the inulin acetate thus obtained could not be caused to solidify. When, however, it is dissolved in absolute alcohol and treated with sodium ethoxide, it gives *trifructose sodium*, $(C_6H_{10}O_5)_3 \cdot NaOH$. The reducing power of the latter towards Fehling's solution is approximately one-third of that of fructose sodium. The corresponding trifructose cannot be precipitated by the addition of alcohol to solutions of trifructose in water which have been neutralised with acetic acid. Attempts to prepare a derivative of it did not meet with success, since phenylbenzylhydrazine gave only fructosephenylbenzylhydrazone.

Inulin sodium has the composition $(C_6H_{10}O_5)_3 \cdot NaOH$, whether obtained by precipitating a solution of inulin in aqueous sodium hydroxide (10%) with alcohol or by the hydrolysis of inulin acetate with sodium ethoxide. The sparingly soluble barium inulin is

constituted similarly. It is, however, pointed out that the method first mentioned for the isolation of the additive compounds of polysaccharides and sodium hydroxide is untrustworthy; the sodium content of such substances depends entirely on the concentration of the sodium hydroxide solution, from which they are precipitated by alcohol or on the quantity of water with which they are treated for the removal of adherent sodium hydroxide. H. W.

An Alkali-soluble Modification of Cellulose. EMIL KNOEVENAGEL and HEDWIG BUSCH (*Cellulosechemie*, 1922, 3, 42—60).—When viscose cellulose is subjected to acid hydrolysis under conditions equivalent to those employed for the preparation of Girard's hydrocellulose, it yields a product which is completely soluble in cold 8% sodium hydroxide solution, even after drying, and is reprecipitated practically without loss on neutralisation. This alkali-soluble cellulose may also be prepared at the ordinary temperature by treating viscose cellulose containing from 2 to 11% of moisture with dry hydrogen chloride. The conversion does not take place if the cellulose is completely dried. Alkali-soluble cellulose contains 8.3% of hygroscopic moisture as compared with 11.0% for viscose cellulose, and has the formula $(C_6H_{10}O_5)_3 \cdot H_2O$; it has the unusually high "copper value" of 12.5—14.0, and forms a phenylhydrazone of indefinite properties containing 4.3% of nitrogen. It has no acid reaction (towards phenolphthalein); when heated with dilute alkali hydroxides it gives a yellow coloration; when boiled with calcium hydroxide for eight hours, it loses 50% in the form of soluble products, but, unlike oxy- and hydro-cellulose under similar treatment, it behaves as a uniform substance, in that the "copper value" of the residue is substantially the same of that of the original material. It resembles viscose cellulose in the fact that it is not readily acetylisable by the usual methods, but it yields a benzoate with the greatest of ease; this is completely soluble in chloroform.

The capacity to form alkali-soluble cellulose is determined by the nature of the previous modification of the cellulose and by the residual affinities released thereby. The formation is proportional to the "hydration value" of the modified cellulose before hydrolysis, as determined by Schwalbe's method (difference between the copper values before and after boiling with 5% sulphuric acid for fifteen minutes). Ordinary hydrocellulose and cellulose regenerated by saponification of cellulose acetate will not yield the alkali-soluble product. Viscose cellulose yields it most readily; strongly mercerised cotton or wood cellulose, on subsequent hydrolysis, yields up to 20%, and the yield may be increased by the more severe action of hot concentrated alkali hydroxides. Wood cellulose when heated for several hours at 140° in an indifferent medium, such as xylene or glycerol, gives substantial yields of alkali-soluble cellulose after subsequent hydrolysis, but the presence of a little moisture during the preliminary heating treatment is essential to ensure the desired type of modification [cf. *J. Soc. Chem. Ind.*, 1922, 458A]. J. F. B.

Behaviour of Oxidised Cellulose. EDMUND KNECHT and F. P. THOMPSON (*J. Soc. Dyers and Col.*, 1922, **38**, 132—136).—Oxidation of cotton cellulose with potassium permanganate in the presence of cold dilute sulphuric acid showed that in the initial stages the consumption of oxygen was approximately proportional to the formation of aldehydic or ketonic groups, as measured by the increase in the "copper value" of the oxidised products. After the expenditure of half an atomic equivalent of active oxygen, however, the increase in "copper value" with further oxidation was very small and, since the more highly oxidised products were to a large extent soluble in alkali hydroxide solution, it is inferred that the later stages of oxidation are complicated by formation of carboxylic acid groups. Acetylation of the original and oxidised celluloses under identical conditions indicated that the oxidised cellulose was esterified more slowly than the original and suffered considerable hydrolysis to products soluble in water. On nitration under identical conditions, the oxidised cellulose yielded products containing in all cases less nitrogen than the nitrates from the original cellulose. Hence it would appear that there is a definite suppression of active hydroxyl functions as the result of oxidation, although this loss is not accurately proportional to the quantity of oxygen consumed. [See also *J. Soc. Chem. Ind.*, 1922, July.] J. F. B.

The Spontaneous Oxidation of Lignin, Natural Humus Material and Coal and the Influence of Alkali thereon. HANS SCHRADER (*Brennstoff-Chemie*, 1922, **3**, [ii], 161—167).—It has been shown previously that lignin is almost completely oxidised to humic acids by heating with sodium hydroxide solution to 200° under pressure. In order to obtain evidence more directly bearing on the possibility of the humus fraction of coal being a decomposition product of lignin, this oxidation was investigated at atmospheric temperature and pressure. A weighed quantity of lignin was placed in a flask covered with 5*N*-sodium hydroxide solution, the flask filled with oxygen, tightly corked, and allowed to remain for forty-six hours. It was then opened, water added, and the whole contents filtered. The humic acids were precipitated from the filtrate by acidification and warming, washed, and dried at 105° in a current of carbon dioxide. They amounted to 9.4% of the (pure) lignin used. The acid filtrate on evaporation to dryness and extraction of the residue with ether yielded a crystalline substance. If the flask was filled with nitrogen instead of oxygen, oxidation proceeded much more slowly, and stopped when 2.3% of humic acids had been formed. A repetition of the above oxidation lasting eight months with 375 grams of pure lignin yielded 192.5 grams of undissolved organic material, 103.5 grams of humic acids, 10.3 grams of non-volatile acids soluble in ether (including 1.62 grams of succinic acid, 0.47 gram of oxalic acid, 0.26 gram of isophthalic acid (?), and an indeterminate quantity of higher benzenecarboxylic acids), and 6.1 grams of non-volatile acids soluble in alcohol. The 62.3 grams loss includes acetic acid, formic acid, water, and carbon dioxide.

The comparative rates of absorption of oxygen by lignin, pine wood sawdust, lignite, cellulose (filter-paper), and coal, each of them as a finely divided suspension in 5*N*-sodium hydroxide solution, were next determined, over a period of a thousand hours with regular shaking, the oxygen being measured from a gas burette. The volume absorbed by 1 gram of substance ranged downwards in the order mentioned above from 82 c.c. with lignin to 6.7 c.c. for coal. In no case had absorption ceased after a thousand hours' treatment, and it was further shown that the absolute results obtained varied with the degree of shaking. The methoxyl content of the humic acid produced in this way was much lower than that of the original lignin, a point of similarity to natural humic acid. The part played by the sodium hydroxide in these oxidations may, it is suggested, be filled in nature by lime or ammonia, whilst bacterial action may also be of importance. The analogy is discussed at length. C. I.

The Colloids Arabic Acid and Arabic Acid plus Gelatin. F. W. TIEBACKX (*Pharm. Weekblad*, 1922, 59, 574-589).—The precipitation of gum and gelatin together from a mixture of solutions, in presence of very dilute acids, occurs for values of p_H between the isoelectric points; for gelatin in presence of hydrochloric acid, this point is about 1×10^{-4} HCl (Hardy), for arabic acid in presence of hydrochloric acid, the isoelectric point is found to correspond with about 2×10^{-3} HCl.

Arabic acid, prepared by repeated precipitation with alcohol and long dialysis, containing no calcium or chlorine, and only 0.1% ash (K_2CO_3), has an equivalent weight 1210, agreeing with O'Sullivan's molecular weight 2418. The formula HAAH is suggested, A being the arabic acid anion. The molecule can be imagined, on the hypothesis of Duclaux, to be $(nHA)AH$, where $n=1$; instead, therefore, of being regarded as a typical colloid, gum really approaches the crystalloid.

By Kohlrausch's method, the conductivity at 18° ($K \times 10^{-4}$) was found to be 8.7. From the alteration of the conductivity on neutralisation, the acid appears to act as a moderately strong monobasic acid. The degree of dissociation of the salts has been measured, but it is extremely difficult to remove traces of electrolytes, which interfere with the determinations; there appears to be no true dissociation constant. The dissociation of the potassium and sodium salts decreases with dilution, passing through a minimum value. S. I. L.

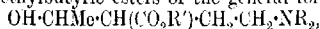
The Solution of Tetramethylammonium Aluminate. JINDŘICH BŘEZINA (*Chem. Listy*, 16, [2], 25-26).—Metallic aluminium is dissolved in a solution of tetramethylammonium hydroxide, and the conductivity of the solution with varying amounts of aluminium is measured. From the measurements thus obtained it is deduced that the aluminium hydroxide produced is neutralised in the same way as by an inorganic base, and that it acts as a monobasic acid, since solution of aluminium ceases when there is present 1 mol. of aluminium hydroxide to one of base. The salt

thus formed is highly dissociated in solution. The transport number for the anion of ortho-aluminic acid is 24 at 0°. R. T.

The Preparation and Properties of Organic Stanno- and Stanni-chlorides. IV. Some Diamine Stannichlorides. J. G. F. Druce (*Chem. News*, 1922, **124**, 310—313).—In continuation of previous work (A., 1919, i, 481), certain diamine stannichlorides have been prepared. *Hydrazine stannichloride* was obtained by mixing stannic chloride and hydrazine hydrochloride in hydrochloric acid. *Methylenediamine stannichloride*, *ethylene-diamine stannichloride*, and *propylenediamine stannichloride* were similarly prepared. Crystallographic data are given for the crystals of propylenediamine stannichloride and for *m*- and *p*-phenylenediamine stannichlorides. All the diamine stannichlorides described are soluble in water with partial hydrolysis and can best be crystallised from hydrochloric acid. W. G.

The Amino-alcohols. Homologues of Novocaine. E. FOURNEAU and J. PUYAL (*Bull. Soc. chim.*, 1922, [iv], **31**, 424—435).—Propylene, butylene, and amylene were prepared by passing the vapours of the corresponding alcohol over infusorial earth at 400°. Starting with a commercial amyl alcohol boiling at 128—130°, the main product was β -methyl- Δ^2 -butylene. These hydrocarbons were converted into the bromohydrins by the action of bromine water, and these in turn by the action of dimethylamine yielded the dimethylamino-alcohols, from which certain derivatives were prepared. The following compounds are described: *Propylenebromohydrin*. β -Bromo- γ -hydroxybutane, $\text{CHMeBr}\cdot\text{CHMe}\cdot\text{OH}$, b. p. 63°/16 mm. and 154°, *d* 1.5016. β -Chloro- γ -hydroxybutane, b. p. 138—140°, and the corresponding Δ^2 -butylene oxide, b. p. 56°. α -Bromo- β -methylbutan- β -ol, $\text{CH}_2\text{Br}\cdot\text{CMeEt}\cdot\text{OH}$, b. p. 67°/18 mm., *d* 1.42. α -Dimethylaminopropan- β -ol, b. p. 45°/20 mm. α -Diethylaminopropan- β -ol, b. p. 157°. β -Dimethylaminobutan- γ -ol, b. p. 53°/18 mm. and 145°. β -Diethylaminobutan- γ -ol, b. p. 74°/16 mm. and 167—174°. α -Dimethylamino- β -methylbutan- β -ol, b. p. 53°/18 mm. and 144—146°. From these amino-alcohols certain substituted benzoyl derivatives have been prepared, namely: *Nitrobenzoyloxydimethylaminopropane hydrochloride*, m. p. 198°. *Nitrobenzoyloxydiethylaminopropane hydrochloride*, m. p. 187°, and the corresponding aminobenzoyl derivative (methylnovocaine), m. p. 150—152°. *Nitrobenzoyloxydiethylaminobutane hydrochloride*, m. p. 148°, and the aminobenzoyl derivative, m. p. 172°. The derivatives obtained from dimethylaminomethylbutanol were shown to be identical with known stavaine derivatives. W. G.

Preparation of β -Aracyl- α -dialkylaminoethylbutyric Esters. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 161539).—Dialkylaminoethyl haloids are caused to react with ethyl sodioacetate, and the resulting ketonic acid esters are reduced, for example, by means of sodium amalgam to β -hydroxy- α -dialkylaminoethylbutyric esters of the general formula,



where R is an alkyl group, and R' an alkyl or aryl group. *Ethyl β-hydroxy-α-diethylaminoethylbutyrate* is a colourless liquid, b. p. 135—136°/10 mm., soluble in water to an alkaline solution. When heated with an aromatic acid chloride, as, for example, benzoyl chloride, the desired aromatic ester is formed, in this case *ethyl β-benzoyl-α-diethylaminoethylbutyrate*, which is a colourless oil forming a crystalline *hydrochloride*, m. p. 130—131°, readily soluble in water, and possessing valuable local anæsthetic properties.

G. F. M.

Explosion of Hydrargyrum Oxycyanatum. E. MERCK (*Pharm. Zentr.-h.*, 1922, **63**, 232—233).—Mercury oxycyanide is liable to explode when ground in a mortar, or rubbed between a glass stopper and the neck of a bottle; explosion has also taken place when the compound has been mixed with indifferent substances by means of a wooden spatula on a wooden board. W. P. S.

Sulphur Thiocyanate. HANS LECHER and MAX WITTMER (*Ber.*, 1922, **55**, [B], 1481—1482; cf. Lecher and Wittmer, this vol., i, 641).—A solution of thiocyanogen in ether reacts readily with dry hydrogen sulphide with the separation of *sulphur thiocyanate*, $S(SCN)_2$, colourless, pearly leaflets which are decomposed by an excess of the gas. The substance decomposes somewhat readily when preserved at the atmospheric temperature. When heated in an open tube in the water-bath it rapidly darkens and then suddenly decomposes with evolution of orange-coloured vapours. A solution of it in a mixture of ether and benzene does not react with powdered iron, but the violet red colour of ferric thiocyanate is immediately developed when a drop of water is added; the substance and also disulphur dithiocyanate (following abstract) are thus distinguished sharply from free thiocyanogen. H. W.

Disulphur Dithiocyanate. HANS LECHER and ALFRED GOEBEL (*Ber.*, 1922, **55**, [B], 1483—1495).—Sulphur chloride reacts with metallic thiocyanates with the formation of *disulphur dithiocyanate*, but the course of the change is greatly dependent on the particular thiocyanate and the solvent. Potassium thiocyanate appears to be quite unsuitable and lead thiocyanate is not dependable, the reaction being governed by unknown catalytic influences. The best and most uniform results are obtained with mercuric thiocyanate. If solutions of the compound are desired, chloroform or carbon tetrachloride are conveniently used as solvents, since they do not dissolve the mercury salts; if, however, the compound is to be isolated, carbon disulphide is to be preferred. For its isolation, the solutions prepared in this solvent are cooled in a mixture of solid carbon dioxide and acetone; the mother-liquor is decanted, the residue is dissolved in ether, from which it is frozen out, and the process is repeated as often as necessary. A special form of apparatus which permits the necessary filtration and manipulation at a low temperature and with the minimum exposure to air is described and figured in the text. Disulphur dithiocyanate forms colourless crystals, m. p. —3·3° (corr.), to an

odourless, yellow, viscous liquid. It is somewhat unstable and shows obvious signs of decomposition after preservation in an ice-chest during about two days. At the atmospheric temperature, its stability appears to be controlled largely by unascertained catalytic influences. When cautiously heated, it becomes successively dark yellow and red, and ultimately detonates. It does not react with iron in the presence of ether, but immediately forms ferric thiocyanate after addition of a drop of water. The isolated liquid substance, on the other hand, reacts instantaneously with iron. In its initial phase the hydrolysis of disulphur dithiocyanate by water appears to be analogous to that of sulphur chloride: $S_2(SCN)_2 + 2H_2O \rightarrow HO\cdot S\cdot S\cdot OH + 2HCNS$, but reaction proceeds subsequently in accordance with the schemes: $HO\cdot S\cdot S\cdot OH + 2HSCN \rightarrow 2S + 2H_2O + (SCN)_2$ and $3(SCN)_2 + 4H_2O \rightarrow 5HSCN + H_2SO_4 + HCN$. Disulphur dithiocyanate reacts with piperidine in the presence of carbon tetrachloride, giving piperidine thiocyanate, $C_5H_{11}N\cdot HSCN$, colourless leaflets, m. p. 95° , and piperidine disulphide, m. p. $64-64.5^\circ$, b. p. $160-161^\circ/11$ mm. The reaction is closely analogous to that which occurs under similar conditions between sulphur chloride and piperidine. When dissolved in carbon disulphide, sulphur chloride reacts with dimethylaniline in such a manner that di-*p*-dimethylaminophenyl disulphide constitutes about three-quarters of the isolated sulphides, the remainder being a mixture of the corresponding mono- and tri-sulphides. With disulphur dithiocyanate under similar conditions, the equilibrium is displaced in the direction of the mono- and tri-sulphides, which in this case compose about two-thirds of the isolated sulphides, the remaining third consisting of disulphide. Free sulphur is not formed in either reaction.

It appears therefore that disulphur dithiocyanate is a type of sulphur haloid intermediate between sulphur bromide and the controversial sulphur iodide. The thiocyno-radicle preserves its stability and halogen nature when united to the $\cdot S\cdot S\cdot$ group. H. W.

Alkylthiol Thiocyanates. II. HANS LECHER and MAX WITTWER (*Ber.*, 1922, 55, [B], 1474-1480; cf. Lecher and Simon, A., 1921, i, 414).—The preparation of further examples of alkylthiol thiocyanates is recorded. The substances appear particularly valuable for synthetic purposes, since the negative substituent has not a pronounced substituting or de-sulphurising action, as is the case with the chlorine atom. They have been applied in the preparation of mixed disulphides.

Ethylthiol thiocyanate, $Et\cdot S\cdot S\cdot C\equiv N$, is prepared by the action of an excess of thiocyanogen dissolved in ether on an ethereal solution of ethyl mercaptan: $EtSH + (SCN)_2 = Et\cdot S\cdot SCN + HSCN$; unused thiocyanogen and thiocyanic acid are removed by washing the ethereal solution with ice-cold water. It is a colourless liquid, b. p. $52^\circ/1.5$ mm., with an exceedingly unpleasant odour. It is very unstable, and becomes noticeably decomposed when preserved during a quarter to half an hour in an ice-chest; it is more stable in dry ethereal solution. *Phenylthiol thiocyanate* like-

wise decomposes readily. It cannot be purified by distillation in a vacuum, and, at the atmospheric temperature, is a yellow liquid which solidifies to a colourless, crystalline solid when strongly cooled. β -Naphthylthiol thiocyanate forms small, pale yellow crystals, m. p. $64.5-65^\circ$ (corr.) after softening at $63-64.5^\circ$; it may be preserved unchanged for several weeks.

Phenyl ethyl disulphide, $\text{EtS}\cdot\text{SPh}$, a colourless liquid with a faint, unpleasant odour, b. p. 123° (corr.)/14 mm., d_{20}^{25} 1.1119, is prepared by the action of an ethereal solution of thiophenol on a solution of ethylthiol thiocyanate in ice-cold ether. β -Naphthyl ethyl disulphide is a pale yellow liquid, b. p. $162^\circ/2$ mm. *Phenyl β -naphthyl disulphide* (from β -naphthylthiol thiocyanate and thiophenol) crystallises in colourless needles, m. p. $75-76^\circ$.
H. W.

Formation of Hydrogen Cyanide from Nitrogen and Hydrocarbons in the Electric Arc. A. KOENIG and W. HUBBACH (*Z. Elektrochem.*, 1922, **28**, 202-223).—The formation of hydrogen cyanide from acetylene and nitrogen in a water-cooled arc under reduced pressure has been investigated. The concentration of acetylene was kept very low. Keeping the rate of flow of the gas mixture constant (3 litres per hour) the consumption of energy by the arc, gas pressure, and composition were systematically varied. It is shown that mixtures containing less than 2 vol.-% of acetylene were quantitatively converted into hydrogen cyanide without any formation of carbon. With higher concentrations of acetylene, there was a considerable separation of carbon, and the yield of hydrogen cyanide was smaller. The energy yield was only 0.5-1.5 grams per kilowatt hour. Further experiments, designed to test the possibility of a commercial synthesis of hydrogen cyanide from nitrogen and hydrocarbons, were carried out at atmospheric pressure in a high tension arc which was rotating in a magnetic field. In these experiments, the rate of flow of the gas mixture was 10, 20, 50, and 100 litres per hour. The following mixtures were passed through the arc: (1) nitrogen with 1-3% acetylene, (2) nitrogen with 1-9% of 50% acetylene-hydrogen mixture, (3) nitrogen with 1-19% of a 1:2 mixture of acetylene and hydrogen, (4) 7:3 nitrogen-hydrogen mixture with 3-11% of acetylene, (5) 1:1 nitrogen-hydrogen mixture with 4-12% of acetylene, (6) nitrogen with 1-5.6% of ethylene and (7) nitrogen with 2-15% of methane. The energy and material yields with various compositions of the mixtures and various rates of flow are plotted on curves. It is shown that with a relatively slow rate of flow, that is, with the highest temperature, methane which shows the least tendency to deposit carbon gives a practically constant yield of 40% hydrogen cyanide irrespective of its concentration within the limits 2-11%. Ethylene and acetylene mixed with hydrogen show definite maxima in the yields at the point where the deposition of carbon commences. Mixtures of pure acetylene with nitrogen give a maximum yield of hydrogen cyanide in the region where there is a heavy deposition of carbon. With a more rapid rate of flow of the gases, the yields are reversed, methane giving a smaller

yield than the other hydrocarbons, and in these circumstances the yield of hydrogen cyanide from ethylene is much poorer, so that high yields may only be obtained when acetylene is used with a high rate of flow. Very good yields, both with respect to energy and material, are obtained when a mixture of 30% of hydrogen and 70% of nitrogen is passed with 7–8% of acetylene at the rate of 20 l. per hour through the arc. In this case, there is no deposition of carbon. With a very rapid rate of flow (up to 100 l. per hour), the energy yield, from mixtures of nitrogen, hydrogen, and acetylene, with a great excess of nitrogen, reaches a maximum of 10–11 grams of hydrogen cyanide per kilowatt hour. J. F. S.

Simple Cyano- and Cyanuric Compounds. III. Malononitrile and its Halogenation. ERWIN OTT and BERNHARD LÖPMANN (*Ber.*, 1922, 55, [E], 1255–1261).—The bromination of malononitrile dissolved in water has been examined by Hesse, who isolated a small amount of a crystalline substance, m. p. 123–124°, which he considered to be dibromomalononitrile, whilst the main product of the action was an oil which could not be purified. A repetition of his experiments has led to different results. The solid material is shown to be dibromosuccinonitrile; exceptional difficulties are encountered in the analysis of this substance, but its constitution is placed beyond doubt by its hydrolysis to dibromosuccinic acid and reduction of the latter to succinic acid. The liquid product consists of dibromomalononitrile, which can be purified readily by distillation under diminished pressure. It has b. p. 49.2°/10 mm., m. p. +3°. It is a highly reactive substance, which is transformed by alkali iodide in neutral aqueous solution into the unstable *di-iodomalononitrile*, and is reduced quantitatively by an acidified solution of potassium iodide to malononitrile and iodine.

The action of chlorine on malononitrile proceeds on similar lines, but the dichloro-compound has a marked tendency to unite with a further molecule of chlorine, with the formation of a tetrachloride; the formation of the latter cannot be avoided by the use of only that quantity of chlorine which is theoretically necessary. The products obtained are *dichloromalononitrile*, a mobile liquid with a very intense odour of chloropierin, b. p. 97°/754 mm., *dichloromalononitrile dichloride*, b. p. 183–184°/759 mm. (slight decomp.), and *dichlorosuccinonitrile*, monoclinic crystals, m. p. 91°, b. p. 156°/15 mm.

Malononitrile can be obtained fairly readily and in considerable quantity if the method of Phelps and Tillotson (*A.*, 1908, i, 757) is followed for the preparation of ethyl cyanoacetate and the latter is transformed into cyanoacetamide (yield 93%) by alcoholic instead of aqueous ammonia. It appears to be a useful solvent for the determination of molecular weight by the cryoscopic method, the mean constant being 50.03.

H. W.

C₁₈ Fatty Acids. V. Molecular Rearrangements in some Derivatives of Unsaturated Higher Fatty Acids. BEN H. NICOLET and JOSEPH J. PELC (*J. Amer. Chem. Soc.*, 1922, 44, 1145–1149).—The unsaturated fatty acids examined readily give

hydroxamic acids, as do the aromatic or saturated fatty acids, and the following were prepared. Oleohydroxamic acid (cf. Morcelli, A., 1908, i, 758); *elaidohydroxamic acid*, m. p. 86°; *ricinoleohydroxamic acid*, m. p. 65°; *linolohydroxamic acid*, m. p. 8–16°; *oleoacetylhydroxamic acid*, m. p. 63°; *oleodiacylhydroxamic acid*, m. p. 64–65°; *elaidoacetylhydroxamic acid*, m. p. 84°; *elaidodiacylhydroxamic acid*, m. p. 82°. These hydroxamic acids undergo the Lossen rearrangement with aqueous alkali, the change not being affected by the double bond. *Di-trans-heptadecylenylcarbamide* has m. p. 59°, *di-cis-heptadecylenylcarbamide* has m. p. 92–93°, *dihydroxyheptadecylenylcarbamide*, m. p. 57.5°, was obtained from λ -acetylricinoleoacetylhydroxamic acid, m. p. 6–8°.

The Lengfeld-Stieglitz rearrangement of the acetylhydroxamic acids with sodium ethoxide also proceeded normally, the corresponding urethane being obtained. *trans-Heptadecylenylurethane* had m. p. 42–43°, and *cis-heptadecylenylurethane* had m. p. 87–88°.

The supposed analogous rearrangement to the carbimide by the action of acetic anhydride was complicated, however, by the fact that a mixture of *cis*- and *trans*-carbimides always resulted, whichever pure hydroxamic was used. These carbimides could not be separated from one another, but were detected by conversion into the corresponding urethanes.

W. G.

The Fluorides of Organo-metallic Compounds. II. Lead Alkyl and Aryl Fluorides. ERICH KRAUSE and ERICH POHLAND (*Ber.*, 1922, 55, [B], 1282–1289; cf. Krause, A., 1919, i, 9; Krause and Becker, A., 1920, i, 340).—Lead alkyl fluorides cannot be prepared by double decomposition between normal potassium fluoride and the necessary lead alkyl haloid, but are obtained by the action of hydrofluoric acid on lead trialkyl hydroxides, the operations being rendered exceptionally unpleasant by the physiological action of the latter substances. They are considerably more stable than the corresponding lead alkyl chlorides, and are therefore the most stable lead alkyl haloids; after a few months, a slight decomposition is generally evident, which is more marked with decreasing weight of the alkyl group. The melting points are very high and cannot be observed, since they lie invariably above the temperature of decomposition. The lead aryl fluorides are prepared by the action of normal potassium fluoride on the lead aryl bromides; they are uniformly sparingly soluble and very stable substances.

Lead trimethyl fluoride, PbMe_3F , is prepared by exactly neutralising a solution of lead trimethyl hydroxide in alcohol with a mixture of hydrofluoric acid (33%) and alcohol and spontaneous evaporation of the solution over phosphoric oxide. It crystallises in long, very slender needles, d_4^{20} 3.53, dcomp. about 305°. In spite of its high temperature of decomposition, it is remarkably readily volatilised, giving a vapour with an intensely unpleasant, metallic odour. The solubilities of the substance in grams per 100 grams of methyl alcohol, ethyl alcohol, benzene, and water at 30° and 50°, respectively, are 8.24 and 99.5; 6.89 and 82.0; 0.028 and 0.87; 5.51

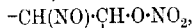
and 26.3. *Lead triethyl fluoride* forms long, thin, doubly refractive prisms, d_4^{25} 2.48, decomp. about 240° ; its solubilities in methyl alcohol, ethyl alcohol, benzene, and water at 30° and 50° are 7.24 and 90.0; 6.11 and 75.1; 0.185 and 0.60; 1.30 and 7.04. *Lead tri-n-propyl fluoride* crystallises in needles, d_4^{25} 1.56, decomp. about 235° , its solubilities in methyl alcohol, ethyl alcohol, benzene, and water at 30.1° and 50.0° , respectively, being 2.01 and 4.94; 1.21 and 3.53; 0.055 and 0.082; 0.17 and 0.23. *Lead tri-isobutyl fluoride* forms long, thin, doubly refracting prisms, d_4^{25} 1.50, decomp. about 230° ; the solubilities in methyl alcohol, ethyl alcohol, benzene, and water at 30.0° and 50.0° , respectively, are 1.76 and 2.96; 1.09 and 2.13; 0.042 and 0.071; 0.12 and 0.18. *Lead tri-isooctyl fluoride*, long, colourless needles, has d_4^{25} 1.46, decomp. about 251° , and the following solubilities in methyl alcohol, ethyl alcohol, benzene, and water at 30.1° and 50.0° : 2.34 and 6.32; 1.73 and 4.55; 0.063 and 0.094; 0.019 and 0.022. *Lead triphenyl fluoride* is prepared by agitating lead triphenyl bromide dissolved in benzene with an aqueous solution of normal potassium fluoride. It forms colourless, microscopic needles, d_4^{25} 1.82, decomp. about 318° . Its solubilities in methyl alcohol, ethyl alcohol, benzene, and water at 30.0° and 50.0° are, respectively, 0.36 and 1.45; 0.15 and 0.24; 0.080 and 0.092; 0.031 and 0.10. *Lead tri-p-tolyl fluoride* crystallises in hair-fine needles, decomp. about 280° . *Lead tricyclohexyl fluoride* forms microscopic spikes, d_4^{25} 1.79, decomp. about 198° . One hundred grams of methyl alcohol, ethyl alcohol, benzene, and water dissolve 0.66, 0.39, 0.11, and 0.096 gram of the substance, respectively, at 30° .
H. W.

Attempt at a Systematic Extension of the Preparation of Organometallic Compounds. Application to Ferrous Ethyl Iodide. ANDRÉ JOB and RENÉ REICH (*Compt. rend.*, 1922, **174**, 1358—1361).—When ferrous iodide in ethereal solution is boiled with zinc ethyl iodide for six hours in the complete absence of air, a solution of *ferrous ethyl iodide*, FeEtI , is obtained. It is quantitatively decomposed by water, giving ethane and ferrous hydroxide, and by absolute alcohol giving ethane and ferrous iodoethoxide. If ferric chloride is used instead of ferrous iodide, the chloride is first instantaneously and quantitatively reduced to ferrous chloride, and this is then slowly converted into ferrous ethyl chloride.

W. G.

Compounds containing Zinc derived from Additive Products of Oxides of Nitrogen and Olefines. ALFRED SCHAARSCHMIDT, MAXIMILIAN VEIDT, and FRANZ SCHLOSSER (*Ber.*, 1922, **55**, [B], 1103—1112).—The olefine, obtained by the action of heat on paraffin chlorinated at 150° (cf. Schaarschmidt and Thiele, A., 1921, i, 1), forms an unstable additive product with nitrogen tetroxide which is reduced by zinc dust and ammonia in alcoholic solution to a mixture of an oil containing nitrogen, a solid paraffin, and a solid product, which contains one atom of zinc for every two atoms of nitrogen. Since the heterogeneous nature of the initial material renders the interpretation of the experimental

results a matter of great difficulty, the behaviour of *cyclohexene* and *cetene* under similar conditions has been investigated. The crude additive product of *cyclohexene* and nitrogen tetroxide is reduced to a mixture of a *liquid*, free from zinc, which could not be purified satisfactorily, but which appears to have the formula $C_6H_{11}O_2N$, and an uncrystallisable *solid* containing nitrogen, oxygen, and zinc in the atomic proportion, 2 : 4 : 1. It appears most probable that the initial additive product is either a nitro-nitrite, $-CH(NO_2) \cdot CH \cdot O \cdot NO$, or a nitroso-nitrate,



which undergoes partial hydrolysis and reduction to the oxime, giving the compound $C_6H_8 \cdot \underset{\text{CH-OH}}{\underset{|}{\text{C}}} \cdot \underset{\text{HO-HC}}{\underset{|}{\text{N}}} \cdot O \cdot Zn \cdot O \cdot \underset{\text{CH-OH}}{\underset{|}{\text{C}}} \cdot \underset{\text{HO-HC}}{\underset{|}{\text{N}}} \cdot C_6H_8$. If this is

decomposed by being treated with hydrogen sulphide in glacial acetic acid solution, it yields the corresponding hydroxy-oxime which resembles closely the zinc-free reduction product. With *cetene*, the results are to some extent similar. The zinc-free *liquid* appears to have the formula $C_{16}H_{33}O_2N$, whereas the solid *product*, yellow crystals, m. p. (indefinite) $90-93^\circ$, has the composition $(C_{16}H_{33}O_2N)_2Zn$. If, however, the latter is crystallised repeatedly from ether, it yields a *substance*, $C_{32}H_{60}O_4N_2Zn$, m. p. $80-81^\circ$, which is converted by hydrogen sulphide in glacial acetic acid solution into a yellow, crystalline *compound*, $C_{16}H_{31}ON$. It appears, therefore, that, in addition to the hydroxy-oxime compound, an unsaturated oxime is also produced which contains the oxime group at the end of the chain.

Cetene-ψ-nitrosite, $C_{22}H_{44}O_6N_4$, colourless crystals, m. p. 85° , is obtained by the gradual admixture of solutions of *cetene* and nitrogen peroxide in light petroleum at -15° to -8° .

Similar series of compounds containing aluminium and mercury in place of zinc have also been prepared. H. W.

The Structure of the Benzene Nucleus. I. Intra-nuclear Tautomerism. CHRISTOPHER KELK INGOLD (T., 1922, 121, 1133-1143).

The Structure of the Benzene Nucleus. II. Synthetic Formation of the Bridged Modification of the Nucleus. CHRISTOPHER KELK INGOLD (T., 1922, 121, 1143-1153).

The Influence of some Substituents in the Benzene Ring on the Mobility of Chlorine in the Side-chain in its Relation to the Problem of Substitution in the Benzene Ring. S. C. J. OLIVIER (*Rec. trav. chim.*, 1922, 41, 301-311; cf. A., 1914, ii, 846).—In the reaction between *p*-bromobenzenesulphonyl chloride and substituted benzenes, the influence of the substituents is found to be $Me > H > Br > Cl > NO_2$, and this is, to a great extent, confirmed by the converse reaction—benzene and substituted sulphonyl chlorides—the result in the latter case being $Me > H > Br > Cl > NO_2$. Similar results are obtained in the case of saponification of benzyl chloride and its ring-substituted derivatives, by a large excess of water. The position of the substituents in addition

to their nature was examined and the above results amplified as follows: $p\text{-Me} > o\text{-Me} > m\text{-Me} > \text{H} > p\text{-Cl} > o\text{-Cl} > m\text{-Cl} > m\text{-NO}_2 > o\text{-NO}_2 > p\text{-NO}_2$. Thus, from knowledge of the substituent and its position, the substitution in the ring may be predicted, and the theoretical results which would be expected from the order given above are in accordance with those obtained by Holleman and his co-workers.

H. J. E.

The Labile Nature of the Halogen Atom in Organic Compounds. IV. **The Tautomeric Hydrogen Hypothesis, and the Removal of the Halogen Atom from Aromatic Nitro-compounds.** ALEXANDER KILLEN MACBETH (T., 1922, 121, 1116—1121).

Physico-chemical Investigation of Tetrahydronaphthalene and Decahydronaphthalene. W. HERZ and PAUL SCHULTAN (Z. physikal. Chem., 1922, 101, 269—285).—The authors have investigated a number of the physical properties of tetralin (tetrahydronaphthalene) and decalin (decahydronaphthalene). These substances are of great use as solvents and are also used as sources of heat and power and have a use as lubricants. The substances were carefully purified and the following physical constants determined: boiling point, tetralin, 207.3° , decalin, 191.7° ; vapour pressure formula, tetralin, $\log p = -2681.3/T + 1.75 \log T - 0.0032147 + 5.31446$; decalin, $\log p = -2395.2/T + 1.75 \log T - 0.002709837 + 4.62719$; heat of vaporisation, tetralin, 79.32 cal./gr., decalin, 71.01 cal./gr.; Trouton constant, tetralin, 21.8, decalin, 21.1; ebullioscopic constant, tetralin, 5773, decalin, 6036; specific heat ($15\text{--}18^\circ$), tetralin, 0.403, decalin, 0.395; melting point, tetralin, $-35.0^\circ \pm 0.5^\circ$, decalin $-124^\circ \pm 2^\circ$; density, tetralin, $d_4 = 0.9843$ ($1-763 \times 10^{-6}$), decalin, $d_4 = 0.8975$ ($1-818 \times 10^{-6}$); coefficient of expansion ($15\text{--}25^\circ$), tetralin 0.00078, decalin, 0.00086; critical temperature, tetralin 789° , decalin, 724° ; measurements of internal friction have been made for both substances at 25° , 50° , and 75° , and the surface tension has been measured at a series of temperatures; at the boiling point the surface tension in dynes/cm. is: tetralin 17.46, decalin 15.71, and the molecular surface energy: tetralin 512.9, decalin 505.1. A number of other quantities are calculated and an account of some partition experiments is given.

J. F. S.

Stereoisomeric Derivatives of Stilbene. R. STOERMER and H. OEHLERT (Ber., 1922, 55, [B], 1232—1243).—The authors describe a series of attempts to convert stable into labile stilbene derivatives by the action of ultra-violet light. In general, the experiments are greatly complicated by the formation of resinous products, and the yields are not good. In all the cases investigated the melting points of the labile are lower than those of the corresponding stable compounds, and the isomerides are not infrequently distinguished by marked differences in colour.

2:4-Dinitrostilbene, $(\text{HPh})_2\text{CH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, is converted by exposure in benzene solution to the rays of a quartz-mercury lamp to the extent of 20% into allo-2:4-dinitrostilbene, large,

transparent, lemon-yellow crystals, m. p. 127°; the solubility of the labile and stable compounds in benzene at 20° is, respectively, 11.79% and 3.7%. 4-Nitro-2-aminostilbene and 2-nitro-4-aminostilbene do not suffer a similar transformation in benzene solution. Their acetyl derivatives are likewise unchanged. The attempted partial reduction of *allo*-2:4-dinitrostilbene by ammonium sulphide in the presence of alcohol results partly in the production of stable 2:4-dinitrostilbene and partly in the formation of stable 2-nitro-4-aminostilbene. Stable 2:4-dinitrostilbene, m. p. 140°, is partly reduced by phenylhydrazine at 100° to 4-nitro-2-aminostilbene, but another portion undergoes a remarkable change to a red, crystalline *variety*, m. p. 140° (m. p. when mixed with the yellow stable 2:4-dinitrostilbene, 140°). Either form, on protracted exposure to sunlight, appears to pass into a brown modification, m. p. 140°, so that here a remarkable instance of colour trimorphism is possibly presented. *allo*-2:4-Dinitrostilbene is transformed by bromine into the dibromide of the stable modification.

The most suitable solvent for the isomerisation of 4-nitrostilbene is chloroform, since resinification occurs to only a slight extent, although the yields of *allo*-4-nitrostilbene, large, brownish-yellow, quadratic crystals, m. p. 65°, leave much to be desired. It is reduced by ferrous sulphate and ammonia to *allo*-4-aminostilbene, which could be isolated only as a yellowish-red liquid. When dissolved in alcohol and treated with hydrochloric acid, it gives the hydrochloride of the stable isomeride, m. p. 245°, but by cautious acetylation or benzoylation it can be transformed into *allo*-4-acetylaminostilbene, yellow crystals, m. p. 134°, and *allo*-4-benzoylamino-stilbene, broad needles, m. p. 154°.

2-Nitro-4-cyanostilbene is converted to a small extent by exposure to ultra-violet light into cyanophenylisatogen, m. p. 224° (cf. Pfeiffer, A., 1916, i, 327).

2-Nitrostilbene-4-carboxylic acid is isomerised to a small extent in benzene solution to *allo*-2-nitrostilbene-4-carboxylic acid, pale yellow, crystalline aggregates, m. p. 158°. The conversion occurs to a greater extent with the esters; *methyl allo*-2-nitrostilbene-4-carboxylate forms coarse, apparently rectangular crystals, m. p. 91°, whereas the corresponding *ethyl* ester could only be obtained as a liquid which, when hydrolysed, gave a mixture of the stereo-isomeric acids.

Stable *methyl 2-aminostilbene-4-carboxylate*, lemon-yellow, flat needles, m. p. 130°, is obtained by the reduction of the corresponding nitro-ester with ferrous sulphate and ammonia; the *diazonium* salt is described. *Methyl allo*-2-aminostilbene-4-carboxylate, large dark yellow or pale brown needles, m. p. 95°, is prepared similarly from the *allonitro*-ester. H. W.

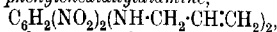
Dinitrodiphenylamine. R. C. MORAN (U.S. Pat. 1401631).—Dinitrodiphenylamine is prepared by combining a halogenodinitrobenzene with aniline by heating to 90–100° with sodium carbonate or sodium hydrogen carbonate in the absence of solvents or added water.

CHEMICAL ABSTRACTS.

Action of certain Primary Bases on 5-Bromo-1:2:4-trinitrobenzene. M. GIUA and A. ANGELETTI (*Gazzetta*, 1922, 52, i, 316—322).—Since 5-bromo-1:2:4-trinitrobenzene contains a nitro-group in the 1-position and a labile hydrogen atom (A., 1921, i, 551), the action on it of bases may give rise to two series of compounds: (1) $C_6H_2Br(NO_2)_3 + 2NH_2R = C_6H_2Br(NO_2)_2 \cdot NHR + NH_2R \cdot HNO_2 \rightarrow R \cdot OH + N_2 + H_2O$, and (2) $C_6H_2Br(NO_2)_3 + 4NH_2R = C_6H_2(NO_2)_2(NHR)_2 + NH_2R \cdot HBr + R \cdot OH + N_2 + H_2O$. In the case of primary aromatic amines, the preceding equations become: (1a) $C_6H_2Br(NO_2)_3 + 3NH_2R = C_6H_2Br(NO_2)_2 \cdot NHR + NR:N \cdot NHR + 2H_2O$ and (2a) $C_6H_2Br(NO_2)_3 + 5NH_2R = C_6H_2(NO_2)_2(NHR)_2 + NR:N \cdot NHR + NH_2R \cdot HBr + 2H_2O$. The reaction (1) or (1a) has been investigated for a number of bases, and reaction (2) for allylamine, 2 mols. of the latter and 1 mol. of the bromonitro-compound yielding an oily product difficult to purify. The negative grouping of 5-bromo-1:2:4-trinitrobenzene causes the nitro-group in position 1 to react first, the bromine atom reacting only when the base is in excess and the heating prolonged.

5-Bromo-2:4-dinitroethylamine, $C_6H_2Br(NO_2)_2 \cdot NH_2Et$, prepared by the action of ethylamine, forms small, lustrous, orange-yellow prisms, m. p. 105—106°, and in alcoholic solution gives a red coloration with alkalis.

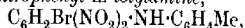
2:4-Dinitro-m-phenylenediallyldiamine,



crystallises in long, lustrous, pale yellow needles, m. p. 130—140°, dissolves in concentrated sulphuric acid with a yellow coloration, and in alcoholic solution gives a brick-yellow coloration with alkalis.

5-Bromo-2:4-dinitrodiphenylamine, prepared from aniline and 5-bromo-1:2:4-trinitrobenzene, forms garnet-red prisms, m. p. 156° (cf. Jackson and Cohoe, A., 1901, i, 585).

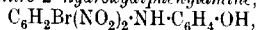
5-Bromo-2:4-dinitrophenyl-m-tolylamine,



obtained by the action of *m*-toluidine, crystallises in red prisms, m. p. 152°, and gives a dark red coloration with either alkalis in alcoholic solution or concentrated sulphuric acid.

5-Bromo-2:4-dinitrophenyl-p-tolylamine, prepared from *p*-toluidine, forms pale yellow prisms, m. p. 164—165°, and gives a red coloration with alkalis in alcoholic solution, and a red solution with hot concentrated sulphuric acid.

5-Bromo-2:4-dinitro-2'-hydroxydiphenylamine,

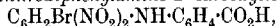


prepared from *o*-aminophenol, forms red prisms, m. p. 203—204°, dissolves in hot, concentrated sulphuric acid giving an intense blue solution, and in alcoholic solution yields a dark red coloration with alkalis.

5-Bromo-2:4-dinitro-3'-hydroxydiphenylamine, $C_{12}H_8O_5N_3Br$, prepared from *m*-aminophenol, crystallises in red prisms, m. p. 173—174°, dissolves in hot, concentrated sulphuric acid to a deep, reddish-brown solution, and in alcoholic solution gives a dark red coloration with potassium hydroxide.

5-Bromo-2 : 4-dinitro-4'-hydroxydiphenylamine, prepared from *p*-aminophenol, forms garnet-red prisms, m. p. 215—216°, gives a brownish-red solution in hot, concentrated sulphuric acid, and in alcoholic solution yields a dark red coloration with alkali.

5-Bromo-2 : 4-dinitrodiphenylamine-2'-carboxylic acid,

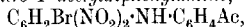


prepared from anthranilic acid, crystallises in garnet-yellow prisms, m. p. 274—276°, forms a yellow solution in hot, concentrated sulphuric acid, and in alcoholic solution gives a reddish-brown coloration with excess of alkali.

5-Bromo-2 : 4-dinitrodiphenylamine-3'-carboxylic acid, prepared from *m*-aminobenzoic acid, forms reddish-yellow needles, m. p. 245°, and gives a red coloration with alkali in excess.

5-Bromo-2 : 4-dinitrodiphenylamine-4'-carboxylic acid, prepared from *p*-aminobenzoic acid, crystallises in lustrous, reddish-yellow prisms, m. p. 247°, and with excess of alkali yields an intense, dark red coloration.

5-Bromo-2 : 4-dinitro-4'-acetyldiphenylamine,



prepared from *p*-aminoacetophenone, forms orange-yellow prisms, m. p. 167—168°, dissolves in cold concentrated sulphuric acid to a red solution, and in alcoholic solution gives a dark red coloration with alkalis.

T. H. P.

The Dihydronaphthalene Series. III. The Oxidation and Bromination of 5 : 8-Dihydro-*a*-naphthylamine. FREDERICK MAURICE ROWE and JOHN STANLEY HERBERT DAVIES (T., 1922, 121, 1000—1007).

Preparation of Amino-phenols or Aromatic Amino-acids.

WILLIAM LEWCOCK, WILLIAM GORDON ADAM, NORMAN EDWARD SIDERFIN, and WILLIAM LYLE GALBRAITH (Brit. Pat. 179753).—Amino-phenols or aromatic amino-acids may be obtained in good yield by the reduction of nitro- or azo-phenols or aromatic acids, with hydrogen sulphide in presence of an alkali carbonate, at about 100°. The compound to be reduced may be dissolved wholly or in part in a solution of the alkali carbonate, or the latter may be added to an already prepared solution of the alkali phenoxide, or salt. The hydrogen sulphide need not be pure but may, for example, be employed in the form of the waste gases from the ammonia scrubbers of gas-works, containing only about 15% of hydrogen sulphide together with a large proportion of carbon dioxide.

G. F. M.

Preparations in the Naphthalene Series. R. SCHOLL [with CHRISTIAN SEER and RICHARD WEITZENBOCK] (*Monatsh.*, 1921, 42, 405—409).—*5-Iodo-1-nitronaphthalene* was prepared by the action of potassium iodide on a solution of 5-nitronaphthalene-diazonium chloride; it forms fine, straw-yellow needles, m. p. 164°. When reduced with tin and hydrochloric acid, it gives *5-iodo- α -naphthylamine*, colourless leaflets, m. p. 75—75.5°. The *sulphate* forms fine needles, becoming red in the air and decomposing at 205—215°. The *hydrochloride* forms fine needles becoming blue

on exposure to light. 5-Iodo- α -naphthol was obtained by boiling a 20% sulphuric acid solution of 5-iodo-1-diazonaphthalene; it is volatile in steam and crystallises from hot water in fine, white needles, m. p. 131–132°. The yield of idonaphthol was small, the principal product being a resin from which a substance, dark red needles, m. p. 228–245°, was obtained, probably a di-iodo-azonaphthol. By methylation of 5-iodo-1-naphthol with methylsulphate in alkaline solution, 5-iodo- α -naphthyl methyl ether was obtained, as needles, m. p. 78–79°. By heating 5-iodo-1-nitronaphthalene with copper powder, 5:5'-dinitro-1:1'-dinaphthyl was obtained, bright brown leaflets, m. p. 228–228.5°.

1:8-Dibromo-2:7-dihydroxynaphthalene was obtained by brominating 2:7-dihydroxynaphthalene in cold acetic acid; it forms aggregates of white needles, m. p. 156–158°, decomposition starting at 130°. Its dibenzoyl derivative forms white needles from acetic acid, m. p. 209°.

[With ARTHUR ERTL.]—5-Nitro- α -naphthonitrile, previously prepared by nitrating α -naphthonitrile, was obtained by the action of potassium cuprocyanide on 5-nitro-1-diazonaphthalene. 5-Nitro-1-diazonaphthaleneimide was also obtained in a new way from 5-nitro-1-diazonaphthalene and hydroxylamine or potassium hydroxylamine sulphonate. The sodium salt of normal 5-nitronaphthalene-1-diazonium hydroxide begins to decompose below 100° and couples with β -naphthol in alkaline solution. The sodium salt of *iso*-5-nitronaphthalene-1-diazonium hydroxide does not couple with alkaline β -naphthol; it forms long, dark yellow needles, decomposing at about 165°.

E. H. R.

The Configuration of Ring Systems in Space. H. G. DERY (*Rec. trav. chim.*, 1922, **41**, 312–342; cf. Böeseken, A., 1921, i, 843).—In applying the boric acid method in order to determine the space configuration of the cyclohexane-1:2-diols, no positive result was obtained (Böeseken and van Giffen, A., 1920, ii, 219), and a further investigation, including also 1:2-diols derived from tetrahydronaphthalene and from cycloheptane, is here reported. The results obtained indicate that homocyclic rings containing more than five carbon atoms exist, not in one plane, but in three dimensions. Of these diols, the isomeride having the lower melting point yields with acetone a condensation product, $C_7H_{12} \begin{smallmatrix} O \\ > \\ O \end{smallmatrix} > CMe_2$, showing it to possess the *cis*-configuration; this is confirmed in the case of the cyclohexanediols by the existence of the *trans*-isomeride in two optically active forms. The two cycloheptane-1:2-diols both form condensation products with acetone (cf. Böeseken and Dery, A., 1921, i, 663), and both increase the conductivity of solutions of boric acid, the increase in the case of the *cis*-isomeride being three times as great as in that of the *trans*-isomeride. The author draws the conclusion that annular tension does not exist in six-atom carbon rings; further, that in all determinations of molecular configuration in the case of rings, the three-dimensional structure should be taken into account.

H. J. E.

a a 2

Catalytic Action of Benzyl Alcohol. J. JACOBSON (*Compt. rend. Soc. Biol.*, 1921, **85**, 299—300; from *Chem. Zentr.*, 1921, iii, 1463).—Benzyl alcohol diminishes the reducing action of Fehling's solution and interferes with the starch-iodide reaction.
G. W. R.

[Preparation of] **Dihydroxyphenylmethylaminoethanol Hydrochloride.** W. N. NAGAI (U.S. Pat. 1399144).—Diacetyl-protocatechualdehyde is condensed with nitromethane in slightly alkaline solution, the product being then reduced with zinc and acetic acid in the presence of formaldehyde, and hydrochloric acid added. The substance is crystalline and has hæmostatic properties.

CHEMICAL ABSTRACTS.

Xanthosterol. H. DIETERLE (*Arch. Pharm.*, 1922, **259**, 244—245).—Xanthosterol, isolated from the bark of *Xanthoxylon Budrunga* is not considered to be identical with lupeol isolated by Goodson (A., 1921, i, 488) from *X. macrophyllum*, as, although the m. p. of xanthosterol, its benzoate, and monobromide lie in each case just below those of lupeol and its corresponding derivatives, xanthosterol cannot be regarded as an impure lupeol, since the mixed melting points do not lie between the melting points of the xanthosterol and lupeol derivatives, but a depression of the m. p. is observed in each case.
G. F. M.

Japanese Bird-lime. II. HIDEKICHI YANAGISAWA and NORIKAZU TAKASHIMA (*J. Pharm. Soc. Japan*, 1922, 179—189; cf. A., 1921, i, 760).—To the product of the saponification of bird-lime prepared from *Trochodendron aralioides* with alcoholic potash were added first dilute alcohol and then water, by which caoutchouc, trochol ($C_{26}H_{44}O_2, \frac{1}{2}C_{22}H_6O, \frac{1}{2}H_2O$), and a small quantity of phytosterol were separated. To the alkaline mother-liquor, a calcium salt was added and the resulting precipitate extracted with ether. From the ether-soluble portion, oleic acid, a semi-liquid acid of unknown nature, resins, trochol, and a phytosterol-like substance were isolated. The latter forms white needles, m. p. 145—155°, and yields two *acetates*, of which the one, $C_{26}H_{43}OAc$, crystallises in white needles, m. p. 190°, and gives on hydrolysis *trochophytosterol*, $C_{26}H_{43}\cdot OH$, m. p. 172—175°; the other forms white needles, m. p. 155—158°. The salt insoluble in ether was decomposed with hydrochloric acid and the liberated acids were converted into their ethyl esters; these proved to be palmitic ester with a small quantity of cerotic ester. By washing the crude ester with sodium carbonate solution, a new acid, *trochic acid*, $C_{31}H_{50}O_2$, was isolated, as a white powder, m. p. 225°; it exists in the bird-lime in the free state. By treatment with acetic anhydride, it gives a substance of m. p. 185—190°.
K. K.

Composition of Bird-lime. II. YUSHICHI NISHIZAWA (*J. Chem. Soc. Japan*, 1922, **43**, 154—172; cf. Yanagisawa, A., 1921, i, 760).—Two alcohols were isolated by saponification of bird-lime. The more fusible *alcohol*, $C_{30}H_{50}O$, forms lustrous scales, m. p. 180°, b. p. 250—255°/0.2 mm., $[\alpha]_D^{20} + 75.77^\circ$, in a mixture of chloroform

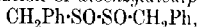
and alcohol; the *acetate* forms colourless scales, m. p. 212° . By oxidation with chromic acid, it gives a crystalline solid, $C_{34}H_{48}O_2$, m. p. 162° , b. p. $270^{\circ}/0.2$ mm. (approx.); it yields an *oxime*, $C_{30}H_{48}O \cdot NOH$, crystallising in needles, m. p. 253° .

The alcohols obtained from bird-lime ($d\ 0.97-0.98$) prepared from *Trochodendron aralioides* were separated as their *acetates*, of which one forms rhombic crystals, m. p. 217° , whilst the other crystallises in needles, m. p. 190° . When hydrolysed, the former gave a dihydric alcohol, *trochodiol*, $C_{29}H_{50}O_2$, crystallising with EtOH from alcohol, rhombic prisms, m. p. 252° , $[z]_D^{20} + 20.3^{\circ}$, in a mixture of chloroform and alcohol, whilst the latter acetate yields a monohydric alcohol, forming needles, m. p. 210° . *Trochodiyyl phenylcarbamate*, $C_{29}H_{48}O \cdot CO \cdot NHPh$, crystallises in rhombic prisms, m. p. 165° .

K. K.

Rupture of Bridge Linkings. CARL WAHL (*Ber.*, 1922, 55, [B], 1449-1457).—Although little systematic work has been done on the subject, the bridge linkings in the ether groups, $:C-O-C:$ and $:C-S-C:$, are generally regarded as very stable. The unstabilising effect of phenyl and acetyl or benzoyl groups on the sulphur bridge is now demonstrated.

Benzyl acetonyl sulphide, $CH_2Ph \cdot S \cdot CH_2 \cdot COMe$, a colourless liquid, b. p. $155-156^{\circ}/17$ mm., is prepared in good yield by the action of sodium benzyl mercaptan on chloroacetone in the presence of alcohol, anhydrous ether, or benzene, and is conveniently purified through the *sodium hydrogen sulphite* compound. It is oxidised with violence by nitric acid to benzaldehyde and sulphuric acid, a similar change being effected by permanganate and glacial acetic acid, or, less readily, by hydrogen peroxide. It is converted by sodium and alcohol into sodium sulphide, and is reduced by sodium in the presence of moist ether or by zinc dust and acetic acid to benzyl mercaptan. An alcoholic solution of the sulphide yields ammonium chloride and benzyl mercaptan when treated with hydroxylamine hydrochloride, but if the effect of the hydrochloric acid is avoided by the addition of sodium acetate, an *oxime* appears to be formed. It readily adds two atomic proportions of bromine without evolution of hydrogen bromide. It gives a colourless, crystalline, additive *compound* with mercuric chloride. When dissolved in cold glacial acetic acid and treated cautiously with hydrogen peroxide (30%), it yields *benzylacetonylsulphoxide*, colourless, lustrous leaflets, m. p. 125° , which is very sensitive towards rise in temperature. The unrestrained action of hydrogen peroxide and glacial acetic acid on the sulphide proceeds vigorously and leads to the formation of *dibenzylsulphoxide*,



m. p. 108° . The sulphide yields a *semicarbazone*, m. p. 123° , and a *phenylhydrazone*, colourless needles, m. p. 155° , which could not be converted into an indole derivative by anhydrous zinc chloride.

Benzyl phenacyl sulphide, $CH_2Ph \cdot S \cdot CH_2 \cdot COPh$, is prepared in 90% yield by the addition of solid phenacyl bromide to sodium benzyl sulphide in the presence of absolute alcohol. It crystallises

in colourless needles which generally melt sharply at 89° , but appears to contain a small proportion of bromine-free impurities which cannot be removed. It gives an additive compound with mercuric chloride. Its behaviour towards oxidising agents is similar to that of benzyl acetonyl sulphide, but it is somewhat less sensitive. It gives a *phenylhydrazone*, needles, m. p. $80\cdot5^\circ$. *Benzylphenacylsulphide* crystallises in colourless leaflets, m. p. 133° .

The sulphides can be converted into sulphones by potassium permanganate and acetic acid if care is taken to avoid the use of an excess of the latter; the yields are satisfactory. *Benzylacetonysulphone*, $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{COMe}$, crystallises in colourless needles, m. p. 89° , whereas *benzylphenacysulphone*, $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{COPh}$, forms colourless, lustrous leaflets, m. p. 113° . The sulphones are transformed by prolonged treatment with boiling alcoholic potassium hydroxide solution (20%) into benzoic or acetic acid and benzylmethylsulphone, m. p. 127° . *Benzylacetonysulphone* gives a *phenylhydrazone*, $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CMe:N}\cdot\text{NHPh}$, needles, m. p. 121° ; a *semicarbazone*, colourless leaflets, m. p. 189° , and an *oxime*, colourless needles, m. p. 151° . The *phenylhydrazone*, slender needles, m. p. $151\cdot5^\circ$, and *oxime*, colourless needles, m. p. 163° , of benzylphenacyl sulphone are described. H. W.

γ -Diallylaminopropyl *p*-Aminobenzoate. O. KAMM and E. H. VOLWILER (U.S. Pat. 1388573).—Diallylamino-esters of aromatic acids containing a benzene nucleus are prepared by dissolving benzyl chloride or a substituted benzyl chloride in benzene, heating for an hour in a reflux apparatus with a diallylamine-alcohol, and then treating the reaction mixture with dilute acid to dissolve basic compounds, and making the aqueous layer alkaline with sodium hydroxide. The ester can be extracted and dissolved in hydrochloric acid. γ -Diallylaminopropyl *p*-aminobenzoate hydrochloride has local anæsthetic properties, and has m. p. 138° ; β -diallylaminopropyl *p*-aminobenzoate hydrochloride has m. p. $158\text{--}160^\circ$.
CHEMICAL ABSTRACTS.

Some Dialkylated Benzyl Cyanides [Phenylacetoneitriles] and the Corresponding Alcohols, Amides, Amines, and Acids. JOSEPH BLONDEAU (*Compt. rend.*, 1922, 174, 1424–1426).—Phenyldialkylacetoneitriles of the type $\text{CPhRR}'\cdot\text{CN}$ were prepared by the method of Bodroux and Taboury by the action of sodamide and the alkyl iodide. α -Phenyl- α -methylbutyronitrile, $\text{CMeEtPh}\cdot\text{CN}$, b. p. $119\text{--}120^\circ/15$ mm. and 239° , and α -phenyl- α -benzylbutyronitrile, $\text{CH}_2\text{Ph}\cdot\text{CEtPh}\cdot\text{CN}$, b. p. $201^\circ/17$ mm., have been prepared. These nitriles on hydrolysis gave first the amides and then the acids, of which α -phenyl- α -methylbutyramide, m. p. 74° , and α -phenyl- α -benzylbutyramide, m. p. 119° ; α -phenyl- α -methylbutyric acid, m. p. 60° , and its methyl ester, b. p. $120^\circ/16$ mm., and ethyl ester, b. p. $124\text{--}125^\circ/14$ mm., and α -phenyl- α -benzylbutyric acid, m. p. 140° , and its methyl ester, m. p. 61° , b. p. $196\text{--}197^\circ/16$ mm., have been prepared. The amides on reduction with sodium and absolute alcohol gave the corresponding alcohols with a certain amount of the corresponding amines. The following are described:— β -phenyl-

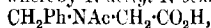
β -ethylbutanol, b. p. 136—137°/13 mm., and 260—261°, giving a benzoyl derivative, b. p. 210°/18 mm., and a phenylurethane, m. p. 70°; β -phenyl- β -methylbutanol, b. p. 138°/23 mm., and 246°, giving a benzoyl derivative, b. p. 202—204°/12 mm., m. p. 46°, and a phenylurethane; β -phenyl- β -benzylbutanol, b. p. 11°/17 mm., giving a benzoyl derivative, and a phenylurethane, m. p. 117°; β -phenyl- β -ethylbutylamine, b. p. 137—139°/23 mm., and its hydrochloride; β -phenyl- β -methylbutylamine, b. p. 112—113°/11 mm., and its hydrochloride; β -phenyl- β -benzylbutylamine, b. p. 193°/10 mm., and its hydrochloride.

W. G.

Synthesis of N-Alkylideneamino-acids and their Conversion into N-Alkylamino-acids by Hydrogenation.

HELMUTH SCHEIBLER and PAUL BAUMGARTEN (*Ber.*, 1922, **55**, [B], 1358—1379).—Somewhat unexpectedly, it has been observed that the condensation of aldehydes with ethyl aminoacetate does not in all cases lead to the production of alkylideneaminoacetic esters in even moderate yield. A more successful synthesis depends on the condensation of the sodium hydrogen sulphite compounds of the requisite aldehyde or ketone with ethyl aminoacetate in accordance with the scheme $\text{CHR}(\text{O}\cdot\text{SO}_2\text{Na})\cdot\text{OH} + \text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} = \text{CHR}(\text{O}\cdot\text{SO}_2\text{Na})\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} + \text{H}_2\text{O}$. The product is subsequently treated with potassium cyanide, giving the cyano-ester, $\text{SO}_2\text{Na}\cdot\text{O}\cdot\text{CHR}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} + \text{KCN} = \text{CN}\cdot\text{CHR}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} + \text{KNaSO}_3$. The latter is transformed by a molecular proportion of alkali hydroxide and alkali ethoxide in absolute ethyl-alcoholic solution into the alkali salt of the alkylideneamino-acid, from which, by hydrogenation, the alkylamino-acid is prepared. It is remarkable that the cyano-esters give the alkylideneamino-acids when acted on by a single equivalent of potassium hydroxide in absolute ethyl-alcoholic solution; the reaction probably occurs in accordance with the scheme $\text{CN}\cdot\text{CHR}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} + \text{KOH} = \text{EtOH} + \text{CN}\cdot\text{CHR}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{K} \rightarrow \text{KCN} + \text{NH}\cdot\text{CH}_2\cdot\text{CO} \begin{smallmatrix} \text{CH}_2\cdot\text{CO} \\ \text{CHR} \end{smallmatrix} \text{O} \rightarrow \text{R}\cdot\text{CH}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The sodium salts of the alkylideneamino-acetic acids are transformed by acetic anhydride or acetyl chloride into N-acetyl compounds, the reaction being expressed by the scheme $\text{CHR}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{Na} + \text{Ac}_2\text{O} = \text{CHR}\cdot\text{NAc} \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix} \text{CO} + \text{AcONa}$.

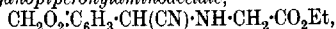
Benzaldehyde reacts energetically with ethyl aminoacetate but the direct isolation of the product of the reaction was not practicable. Reduction of the crude substance with aluminium amalgam in moist ethereal solution or with sodium and alcohol leads to the production of ethyl benzylaminoacetate, b. p. 175—179°/50 mm., the identity of which is confirmed by its conversion into benzylglycine hydrochloride, m. p. 214—216° (corr., decomp.). Simultaneous reduction and acetylation is effected by alternate addition of sodium amalgam and acetic anhydride to an aqueous suspension of the crude product whereby N-acetyl-N-benzylglycine,



colourless aggregates of needles, m. p. 126.5° (corr.), is produced. (See also below.) As judged from the quantity of the reduced ester obtained, the yield of condensation product does not exceed 19% of that theoretically possible. The condensation of piperonal with ethylaminoacetate follows a similar course; the crude product is transformed by successive reduction and treatment with hydrochloric acid into *piperonylglycine hydrochloride*, small, colourless leaflets, m. p. 224° .

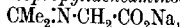
A suspension of benzaldehyde sodium hydrogen sulphite in water is treated with ethyl aminoacetate at 0° and a concentrated aqueous solution of potassium cyanide is subsequently added; *ethyl cyano-benzylaminoacetate*, $\text{CN}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, separates as a pale yellow liquid which cannot be distilled without decomposition, even under diminished pressure, and is identified as the hydrochloride, m. p. 83.5° (corr., decomp.). [Stadnikof (A., 1909, i, 106) gives m. p. 82° .] The yield is 97% of that theoretically possible. The nitrile ester is converted by cold, concentrated sulphuric acid into the *amido-ester*, $\text{NH}_2\cdot\text{CO}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, colourless, lustrous needles, m. p. 135° . The latter is hydrolysed completely with evolution of ammonia by sodium hydroxide, but only the ester group is affected by treatment with a hot aqueous suspension of freshly precipitated copper hydroxide which forms the *copper salt*, $(\text{NH}_2\cdot\text{CO}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O})_2\text{Cu}$, sky-blue, anhydrous crystals. *Benzylideneglycine*, $\text{CHPh}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is obtained by the action of sodium hydroxide or preferably potassium hydroxide on the cyano-ester in absolute ethyl-alcoholic solution, but the brown, viscous syrup which solidifies to a glassy mass cannot readily be purified from sodium or potassium cyanide. *Sodium benzylideneaminoacetate*, a colourless, crystalline powder, is prepared in quantitative yield by the action of equivalent quantities of sodium hydroxide and ethoxide on the cyano-ester; it is somewhat unstable and is readily hydrolysed by warm water, with the production of benzaldehyde. The corresponding *silver, copper, barium, and calcium salts* are described. *N-Acetyl-N-benzylidenebetaine*, $\text{CHPh}\cdot\text{N}\cdot\text{Ac}\cdot\text{C}(\text{CH}_2)_2\text{CO}$, colourless, lustrous needles, has m. p. $103-104^{\circ}$; it is hydrolysed by boiling water to benzaldehyde and aceturic acid, m. p. 206° . *N-Benzylideneglycine* is reduced by sodium and boiling ethyl alcohol to *N-benzylglycine hydrochloride*, m. p. $214-216^{\circ}$ (corr.), whereas its sodium salt is transformed by sodium amalgam and acetic anhydride into *N-acetyl-N-benzylglycine*, m. p. 126.5° (corr.) (see above).

Ethyl N- α -cyanopiperonylaminoacetate,



is a viscous, yellow liquid which is characterised as the *hydrochloride*, a colourless, crystalline powder, m. p. $150-152^{\circ}$ (corr.) after incipient decomposition at about 115° in a sealed capillary. Its conversion into 3:4-methylenedioxybenzylideneglycine, a pale brown, viscous syrup which solidifies to a glassy mass, and *sodium piperonylideneaminoacetate* and the reduction of the latter to *N-piperonylglycine hydrochloride*, small, colourless needles, m. p. 224° (corr., decomp.), are described.

A similar series of changes starting from acetone sodium bisulphite leads to the production of *ethyl N-α-cyanoisopropylaminoacetate*, $\text{CN} \cdot \text{CMe}_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, an almost colourless liquid [hydrochloride, small, colourless crystals, m. p. 87° (corr.) in a sealed capillary], of *sodium N-isopropylideneaminoacetate*,



a colourless, finely crystalline, very hygroscopic powder, and of *N-isopropylglycine hydrochloride*, colourless, lustrous, hygroscopic crystals, m. p. $203\text{--}204.5^\circ$ (corr.) after previous softening, from which *isopropylglycine*, hard irregularly-shaped crystals, m. p. $192\text{--}193^\circ$ (corr., decomp.), is prepared by the action of moist silver oxide.

H. W.

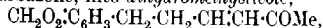
3-Hydroxy-*o*-toluic Acid. YASUHIKO ASAHINA and YOSHIO KONDO (*J. Pharm. Soc. Japan*, 1922, 264—271).—3-Hydroxy-*o*-toluic acid was obtained by the fusion of hydrangenol and phylloulcin with potassium hydroxide, and was also prepared from 4-bromo-*o*-toluic acid by Jacobsen's method. Finally, 3-nitro-*o*-toluic acid, m. p. $151\text{--}152^\circ$, was reduced to the corresponding amino-acid, m. p. $125\text{--}126^\circ$, which was diazotised and boiled with dilute hydrochloric acid, when 3-hydroxy-*o*-toluic acid, m. p. $169\text{--}170^\circ$, was formed, and proved to be identical with that from hydrangenol and phylloulcin. This process is somewhat tedious, and gives a smaller yield than that obtained by Jacobsen's method.

K. K.

The Catalytic Hydrogenation of Methysticin. H. GOEBEL (*Ber. deut. Pharm. Ges.*, 1922, 32, 115—124).—By the catalytic hydrogenation of methysticin,



only the double bond adjacent to the benzene nucleus is eliminated, with the formation of *dihydromethysticin*, m. p. $117\text{--}118^\circ$, which on hydrolysis with alcoholic potassium hydroxide gives the corresponding *dihydromethystic acid*, yellow needles, m. p. $133\text{--}134^\circ$. The constitution of the latter follows from its conversion, on oxidation with alkaline permanganate, into methylenedioxyphenylpropionic acid, m. p. 172° . That the keto-group of methysticin remains unchanged during the hydrogenation is shown by converting dihydromethysticin, which itself, like methysticin, gives no semicarbazone, into *dihydromethysticole*,



by boiling dihydromethystic acid with 5% hydrochloric acid. The ketone boils at $195\text{--}200^\circ/13\text{ mm.}$, and gives a *semicarbazone*, m. p. $149\text{--}150^\circ$. Although dihydromethysticin itself could not be further hydrogenated, the potassium salt of dihydromethystic acid, or of methystic acid, was converted into *tetrahydromethystic acid* by hydrogen and a palladium catalyst. This substance forms white needles, m. p. $137\text{--}138^\circ$, and was converted by boiling with 5% hydrochloric acid into *tetrahydromethysticole*, an oily liquid, b. p. $200\text{--}210^\circ/13\text{ mm.}$, forming a *semicarbazone*, m. p. $164\text{--}165^\circ$. The hydrogenation of the potassium salt of methystic acid takes place in two stages, and by using an old partly poisoned

aa*

catalyst the intermediate *dihydromethystic acid* was isolated. It formed fine needles, m. p. 140—141°, and, as on oxidation it gave piperonal and piperonic acid, it is evident that in this case it is the double bond of methysticin farthest removed from the benzene nucleus that has been eliminated by the hydrogenation. On boiling with 15% hydrochloric acid, *dihydromethystic acid*, b. p. 140—150°/10 mm., was obtained. Its *semicarbazone* melts at 160—161°.

G. F. M.

The Aldehydosalicylic Acids and their Derivatives. EDWARD JOHNSON WAYNE and JULIUS BEREND COHEN (T., 1922, 121, 1022—1029).

The Formation of Cyclic Compounds from Hydroaromatic Dicarboxylic Acids. A. WINDAUS and W. HÜCKEL (*Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, 1920, 11, [ii], 181—187).—Baeyer's strain theory explains the well-known stability of alicyclic compounds with five and six atoms in the ring, especially noticeable with dicarboxylic acids heated at 300° with acetic anhydride. In this paper, the reaction is applied to hydroaromatic dicarboxylic acids, with the view of determining their constitution and the applicability of Baeyer's theory. *cis*- and *trans*-cyclohexane-1:2-dicarboxylic acid gave two different inner anhydrides, the *trans* changing to the *cis* form at higher temperatures. Homophthalic acid prepared by the oxidation of indene with potassium permanganate (Heusler and Schieffer, A., 1899, i, 365) forms white crystals, m. p. 178°, and may be catalytically reduced to *trans*-2-carboxycyclohexane-1-acetic acid, clustered prisms from water, m. p. 146° (*dianilide*, fine needles, m. p. 252°). By heating with acetic anhydride at 240° and distilling at 25 mm., a crystalline distillate was obtained of which the portion soluble in light petroleum gave an anhydride, m. p. 38°; on recrystallisation from water, probably *cis*-2-carboxycyclohexane-1-acetic acid, m. p. 128—129°, was obtained. The latter, therefore, behaves towards Blanc's reaction like an acid of the glutaric series. *o*-Carboxy- β -phenylpropionic acid, obtained by the oxidation of Δ^1 -dihydronaphthalene with potassium permanganate (Straus and Lemmel, A., 1913, i, 256), on catalytic hydrogenation gave an acid, m. p. 103° (*dianilide*, lustrous leaves, m. p. 159°), which, when slowly heated, gave probably *trans*-2-carboxycyclohexane-1-propionic acid, m. p. 143° (*dianilide*, m. p. 205—206°). When heated with acetic anhydride, the acid, m. p. 103°, gave a distillate which, when treated with ether and sodium carbonate, yielded *hexahydro- α -hydrindone*, b. p. 216°/758 mm., in 55% yield [*semicarbazone*, clustered needles from alcohol, m. p. 214—215° (decomp.); *oxime*, m. p. 79—80°]. Thus, *cis*-2-carboxycyclohexane-1-propionic acid under Blanc's reaction behaves like an acid of the adipic series.

CHEMICAL ABSTRACTS.

The Two Isomeric Phthalyl Chlorides. JULIUS VON BRAUN and WILHELM KAISER (*Ber.*, 1922, 55, [B], 1305—1310).—The physico-chemical investigations of Ott (A., 1912, i, 828) have

enabled satisfactory formulæ to be ascribed to the two phthalyl chlorides, but, apart from a recent observation by Pfeiffer (this vol. i, 341), scarcely any chemical differences between the two isomerides have been noted. The author has therefore examined their behaviour towards the salts of dithiocarbamic acid which have been shown previously (A., 1904, i, 90) to react readily with the normal acid chloride complex in accordance with the equation $R\cdot COCl + NR_2H, HS\cdot CS\cdot NR_2 = NR_2H, HCl + R\cdot CO\cdot S\cdot CS\cdot NR_2$. The intensely coloured dithiourethanes immediately decompose in the case of the chlorides of fatty acids in accordance with the scheme $R\cdot CO\cdot S\cdot CS\cdot NR_2 = R\cdot CO\cdot NR_2 + CS_2$, whereas the aryl compounds are rather more stable. *s*-Phthalyl chloride would therefore be expected to give a dark yellow thio-derivative, $C_6H_4(CO\cdot S\cdot CS\cdot NR_2)_2$, which would possess some degree of stability. The behaviour of the *as*-chloride can be predicted with less certainty, but it appears most probable that colourless or faintly coloured, very unstable substances of the type $C_6H_4 < \begin{smallmatrix} C(S\cdot CS\cdot NR_2) \\ CO \end{smallmatrix} > O$ would be initially formed which would decompose primarily into unsymmetrical phthalamides, $C_6H_4 < \begin{smallmatrix} C(NR_2)_2 \\ CO \end{smallmatrix} > O$, from which the symmetrical derivatives would immediately be obtained. The predictions are completely fulfilled by experiment.

The cautious addition of *s*-phthalyl chloride to an ice-cold mixture of piperidine, water, and carbon disulphide causes the separation of *N*-piperidyl-*s*-phthalyl-dithiourethane, $C_6H_4(CO\cdot S\cdot CS\cdot C_5NH_{10})_2$, a brilliant yellow powder, m. p. 123°, which is converted slowly in the cold, but rapidly on warming into carbon disulphide and phthalyl-*NN'*-dipiperidide, $C_6H_4(CO\cdot C_5NH_{10})_2$, m. p. 52–54°, which is identical with the product obtained from *s*-phthalyl chloride and piperidine by the Schotten-Baumann reaction. When *as*-phthalyl chloride is treated in a similar manner, a very faint yellow coloration is developed; the products of the change are piperidine hydrochloride and phthalyl-*NN'*-dipiperidide. Exactly analogous observations are made when piperidine is replaced by dimethylamine. The symmetrical chloride gives *N*-dimethyl-*s*-phthalyl-dithiourethane, a yellow powder, m. p. 107°, which is readily converted into carbon disulphide and *NN'*-tetramethyl-phthalamide, $C_6H_4(CO\cdot NMe_2)_2$, colourless crystals, m. p. 121–122°. With *as*-phthalyl chloride only a very pale yellow colour is developed and the products of the action are dimethylamine hydrochloride and tetramethylphthalamide.

H. W.

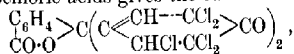
Chloro- and Bromo-derivatives of Phenolphthalein. A. THIEL and FR. MÜLLER (*Ber.*, 1922, 55, [B], 1312–1321; cf. Thiel, A., 1914, ii, 285).—The authors have commenced a study of the influence of systematic halogenation of phenolphthalein on its behaviour as indicator. The present communication deals with substances containing chlorine or bromine in the side nuclei. The usual method for the preparation of phenolphthaleins (condensation of phthalic anhydride with phenols in the presence of a suitable

agent) cannot be utilised in these cases, since it is too largely dependent on unknown and at present uncontrollable factors, and, further, can only lead usefully to symmetrical derivatives. The general method consists in condensing 4'-hydroxybenzoylbenzoic acid or a halogenated derivative of it with phenol or a halogenated phenol in the presence of stannic chloride. 4'-Hydroxybenzoylbenzoic acid is prepared conveniently from phenolphthaleinoxime, which is smoothly hydrolysed by dilute sulphuric acid into the ketonic acid and *p*-aminophenol. Application of the reaction to unsymmetrically substituted halogenated phenolphthaleins shows that the oxime nitrogen in the form of the amino-group is eliminated in combination with the nucleus which is free from or contains least halogen.

The full description of the behaviour of halogenated phenolphthaleins as indicators is recorded elsewhere. It may, however, be noted that the tintorial power diminishes regularly with increasing halogen content to such an extent that the maximal coloration produced in aqueous solution at the atmospheric temperature by a tetrahalogenated compound is only one-hundredth of that produced by phenolphthalein. The tint developed in alkaline solution is not appreciably affected as long as one side nucleus remains unsubstituted, but becomes violet and finally bluish-violet when both rings are substituted.

The following substances are described: *o*-3':5'-Dichloro-4'-hydroxybenzoylbenzoic acid, colourless crystals, m. p. 241°; *o*-3':5'-dibromo-4'-hydroxybenzoylbenzoic acid, m. p. 248°; *o*-3'-chloro-4'-hydroxybenzoylbenzoic acid, colourless crystals, m. p. 212°; 3'-chlorophenolphthalein, m. p. 201° (the melting points of the phthaleins described in this communication are all somewhat indefinite owing to decomposition); 3'-bromophenolphthalein, m. p. 118°; 3':5'-dichlorophenolphthalein, a colourless powder, m. p. 220°; 3':5'-dibromophenolphthalein, a pale yellow, crystalline powder, m. p. 238°; 3':5':3''-trichlorophenolphthalein, a colourless substance, m. p. 122°; 3':5':3''-tribromophenolphthalein, a colourless compound, m. p. 124°.

Chlorination of a suspension of phenolphthalein in glacial acetic and fuming hydrochloric acids gives the substance



m. p. 218°, which is reduced by tin and hydrochloric acid to 3':5':3'':5''-tetrachlorophenolphthalein, m. p. 225°. Its constitution follows from the observation that it is converted by the oxime fusion into *o*-3':5'-dichloro-4'-hydroxybenzoylbenzoic acid.

H. W.

The Structure of Disalicylaldehyde. ROGER ADAMS, M. F. FOGLER, and C. W. KREGER (*J. Amer. Chem. Soc.*, 1922, **44**, 1126-1133).—Disalicylaldehyde is considered to have the constitution shown in the formula IV, and may be called 5:11:13-dibenzo-bisdioxan. The mechanism for the formation from salicylaldehyde is considered to be as follows:

respond to the reactions for cobaltous ions and must be regarded as highly stable complex salts of the type $\begin{matrix} R^1 \cdot C \cdot NO \\ R^2 \cdot C \equiv O \end{matrix} > Co < \begin{matrix} NO \cdot C \cdot R^1 \\ O \equiv C \cdot R^2 \end{matrix}$ in which the co-ordination number of the cobalt is 4.

It is therefore evident that Tschugaev's considerations on tervalent cobalt compounds of the α -oximinoketones are valueless. Further, as the author has obtained the cobaltous salts of oximinoacetylacetone and oximinoacetophenone and has confirmed the existence of the cobaltic salt of α -benzilmonoxime, the configurations of the oximino-compounds cannot, contrary to Tschugaev's suggestion, be related to their capacity to form metallic salts. Indeed, oximinoacetylacetone does not exist in geometrical isomerides, whilst oximinoacetophenone has the β - or anti-structure and α -benzilmonoxime the syn-form.

The cobaltous salt of oximinoacetylacetone, $Co(ON \cdot CAc \cdot CO \cdot CH_3)_2$, crystallises in large, blood-red prisms, m. p. 164° , and dissolves easily in the cold in concentrated sulphuric acid and in sodium or ammonium hydroxide solutions, giving a dark orange-red coloration.

Cobaltous oximinobenzoylacetone, $Co(ON \cdot CAcBz)_2$, forms flattened, orange-brown needles, m. p. 220° (decomp.), and dissolves in cold concentrated sulphuric acid or sodium or ammonium hydroxide, forming yellow solutions.

Cobaltous oximinoacetophenone, $Co(ON \cdot CHBz)_2$, forms orange-brown laminæ, begins to change at about 100 – 120° , and decomposes, sometimes violently, at 240 – 244° , with sublimation of benzoic acid; it dissolves in cold concentrated sulphuric acid to an orange-red solution, but is insoluble in sodium or ammonium hydroxide solution.

Cobaltic α -benzilmonoxime, $Co(ON \cdot CPhBz)_3$, obtained, but not described, by Tschugaev (*loc. cit.*), crystallises in reddish-brown prisms and decomposes violently at 195° or sometimes at a somewhat higher temperature; it dissolves in cold concentrated sulphuric acid to a reddish-brown solution, but is insoluble in potassium or ammonium hydroxide solution.

Cupric oximinoacetylacetone, $Cu(ON \cdot CAc)_2$, obtained similarly to the preceding salts, forms an olive-green powder, decomposes violently at about 140° , and dissolves in sodium hydroxide solution, giving a greenish-yellow, in ammonia solution a greenish-blue, in dilute hydrochloric acid a yellow, and in dilute acetic acid a green, coloration. As it gives some of the reactions of cupric ions, it must be regarded as a less stable complex salt than the cobaltous salts of the α -oximinoketones.

T. H. P.

Two $\alpha\alpha\beta\beta$ -Substituted Propiophenones and their Products of Decomposition by Sodamide. (MME) PAULINE RAMART and G. ALBESCO (*Compt. rend.*, 1922, **174**, 1289–1291).—Substituted ketones of the types $CHPh_2 \cdot CR_2 \cdot C(Ph)Ph$ and $CHPhEt \cdot CR_2 \cdot C(Ph)Ph$ may be prepared by the condensation of mixed organo-magnesium derivatives with phenyl styryl ketones and alkylation of the resulting compounds by means of sodamide. In the alkylation the first alkyl group is introduced easily, but the second only with difficulty.

$\beta\beta$ -Diphenylpropiofenone gives with sodamide and methyl iodide first $\beta\beta$ -diphenyl- α -methylpropiofenone and then $\beta\beta$ -*di-phenyl- $\alpha\alpha$ -dimethylpropiofenone*, m. p. 90° . Under similar conditions, β -phenyl- β -ethylpropiofenone gives β -phenyl- $\alpha\beta$ -diethylpropiofenone, m. p. 68° , and β -phenyl- $\alpha\alpha\beta$ -triethylpropiofenone, b. p. $180^\circ/10$ mm. Both these ketones are decomposed by sodamide, two reactions occurring to almost equal extent, namely:

$$\begin{aligned}\text{CHPh}_2\cdot\text{CR}_2\cdot\text{COPh} + \text{NH}_2\text{Na} &\rightarrow \text{CHPh}_2\cdot\text{CR}_2\cdot\text{CO}\cdot\text{NH}_2 + \text{C}_6\text{H}_6 \\ \text{CHPh}_2\cdot\text{CR}_2\cdot\text{COPh} + \text{NH}_2\text{Na} &\rightarrow \text{CHPh}_2\cdot\text{CHR}_2 + \text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}_2.\end{aligned}$$

Thus $\beta\beta$ -diphenyl- $\alpha\alpha$ -dimethylpropiofenone gave $\gamma\gamma$ -diphenyl- β -methylpropane, b. p. $145^\circ/13$ mm., benzamide, $\beta\beta$ -diphenyl- $\alpha\alpha$ -dimethylpropionic acid in the form of its amide and some tetraphenylethane. β -Phenyl- $\alpha\alpha\beta$ -triethylpropiofenone gave δ -phenyl- γ -ethylhexane, $\text{CHPhEt}\cdot\text{CHEt}_2$, b. p. $205^\circ/740$ mm., benzamide and β -phenyl- $\alpha\alpha\beta$ -triethylpropionic acid, m. p. 82° . W. G.

The Reactivity of Doubly-conjugated Unsaturated Ketones.

III. Unsymmetrical Hydroxy- and Methoxy-derivatives.

JOHANNES SYBRANDT BUCK and ISIDOR MORRIS HEILBRON (T., 1922, 121, 1095—1101).

o-Quinones and 1 : 2-Diketones. V. Benzils of the Super-oxide Type [ψ -Benzils]. A. SCHÖNBERG and O. KRAEMER (Ber., 1922, 55, [B], 1174—1194).—In general, the benzils are yellow substances, but 4 : 4'-diethoxybenzil (Vorländer, A., 1911, i, 865) and 2 : 2'-dimethoxybenzil (Irvine, T., 1907, 91, 541) are colourless. Further examination of these and similar substances has disclosed the existence of a class of benzils in which the dicarbonyl group is present in the peroxide form, $\begin{smallmatrix} \text{R}\cdot\text{C}\cdot\text{C}\cdot\text{R} \\ | \quad | \\ \text{O}\cdot\text{O} \end{smallmatrix}$. These com-

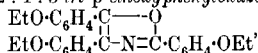
pounds are colourless, but melt to a yellow liquid and give yellow solutions. The phenomenon is reversible since colourless crystals are deposited when the yellow solutions are concentrated or cooled. It can be explained by the assumption of a reversible transformation of the peroxide into the ketonic form. The colourless compounds are converted by solution in concentrated sulphuric acid into intensely coloured derivatives of the ketonic modification. The colourless benzils react very slowly with and are sometimes almost inactive towards the typical dicarbonyl reagents such as *o*-diamines. In contrast to the coloured benzils which contain the dicarbonyl group in the ketonic form, the colourless substances are very stable towards hydrogen peroxide in acid solution.

2 : 2'-Dimethoxy-5 : 5'-dimethylbenzil, colourless leaflets, m. p. 183° , is prepared by the oxidation of a boiling alcoholic solution of the corresponding benzoin with Fehling's solution. It is converted by phenylhydrazine into the corresponding *osazone*, $\text{C}_{30}\text{H}_{30}\text{O}_2\text{N}_4$, yellow crystals, m. p. 197° . It is not affected by aqueous or ethereal ammonia at 200° and does not condense with *o*-phenylenediamine or naphthalene-1 : 2-diamine. It is converted by a boiling mixture of glacial acetic and aqueous hydrobromic acids (50%) into 2-hydroxy-2'-methoxy-5 : 5'-dimethylbenzil, prisms, m. p. (indefinite) 113° ,

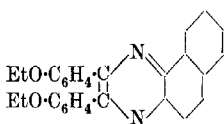
which is re-converted into the dimethoxy-compound by treatment with methyl sulphate.

2 : 2'-Dimethoxybenzil, m. p. 130° (cf. Irvine, *loc. cit.*), is similarly prepared by the oxidation of 2 : 2'-dimethoxybenzoin with Fehling's solution. It gives a *dioxime*, colourless prisms, decomp. 235° (indefinite), and a *diphenylosazone*, $C_{26}H_{26}O_2N_4$, yellow prisms, m. p. 198—199°. It is stable towards aqueous ammonia and *o*-diamines. With hydrobromic and acetic acids it yields 2-hydroxy-2'-methoxybenzil, colourless, lustrous prisms, m. p. 120°.

4 : 4'-Diethoxybenzil (cf. Vorländer, *loc. cit.*) is conveniently prepared by the action of aluminium chloride on a solution of phenetole and oxalyl chloride in carbon disulphide. It is converted by drastic treatment with concentrated aqueous ammonia into *p*-ethoxybenzoic acid and 2 : 4 : 5-tri-*p*-ethoxyphenyloxazole,



colourless needles, m. p. 82°. With naphthalene-1 : 2-diamine in boiling glacial acetic acid solution it slowly gives 2 : 3-di-*p*-ethoxy-



phenyl- $\alpha\beta$ -naphthaquinoline (annexed formula), needles, m. p. 155°. It is converted by a mixture of nitric acid (*d* 1.48) and sulphuric acid (*d* 1.70) into 3 : 3'-dinitro-4 : 4'-diethoxybenzil, lustrous, yellow leaflets, m. p. 216°, which is transformed by naphthalene-1 : 2-diamine hydro-

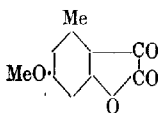
chloride into 2 : 3-di-*m*-nitro-*p*-ethoxyphenyl- $\alpha\beta$ -naphthaquinoline, yellow needles, m. p. 178°. 3 : 3'-Dibromo-4 : 4'-diethoxybenzil crystallises in pale yellow needles, m. p. 208°. 4 : 4'-Dihydroxybenzil, m. p. 235°, after previous softening (*dibenzoate*, yellow needles, m. p. 170°) can be obtained only with difficulty and in poor yield by the action of hydrobromic acid on 4 : 4'-diethoxybenzil, but is readily prepared by the corresponding treatment of 4 : 4'-dimethoxybenzil.

Ethylbenzene is converted by oxalyl chloride and aluminium chloride in the presence of carbon disulphide into *p*-ethylbenzoic acid instead of the desired 4 : 4'-diethylbenzil.

Diphenyl ether is transformed by oxalyl chloride into 4 : 4'-di-*p*-ethoxybenzil, pale yellow, silky leaflets, m. p. 116°, in which the position of the phenoxy groups is established by its oxidative hydrolysis by hydrogen peroxide to *p*-phenoxybenzoic acid, m. p. 159°. With *o*-tolylenediamine hydrochloride, the benzil yields 2 : 3-di-*p*-phenoxyphenyl-6-methylquinoline, yellow aggregates of prisms, m. p. 149°, whilst with naphthalene-1 : 2-diamine hydrochloride it gives 2 : 3-di-*p*-phenoxyphenyl- $\alpha\beta$ -naphthaquinoline, yellow crystals, m. p. 137°.

Oxalyl chloride and 3 : 5-dimethoxytoluene give 6-methoxy-4-methyl-2 : 3-diketocoumaran (annexed formula), lustrous, yellow crystals, m. p. 165°; the same compound is obtained by the similar treatment of 5-hydroxy-3-methoxytoluene.

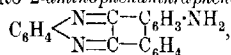
In contrast to the colourless 2 : 2'-dimethoxybenzil and 2 : 2'-dimethoxy-5 : 5'-dimethylbenzil,



the yellow diketones, 4:4'-dimethyl-, 4:4'-dimethoxy-, and 3:4:3':4'-dimethylenedioxy-benzils react readily with naphthalene-1:2-diamine hydrochloride in boiling glacial acetic acid solution, giving, respectively, 2:3-di-*p*-tolyl- $\alpha\beta$ -naphthaquinoline, needles, m. p. 183°, 2:3-di-*p*-methoxyphenyl- $\alpha\beta$ -naphthaquinoline, yellow needles, m. p. 161°, and 2:3-di-*mp*-methylenedioxyphenyl- $\alpha\beta$ -naphthaquinoline, yellow crystals, m. p. 205°.

Piperil is converted by aqueous ammonia at 120° into 2:4:5-tri-*mp*-methylenedioxyphenyloxazole, $\text{N} \ll \text{C}(\text{C}_6\text{H}_3\text{:O}_2\text{CH}_2)\text{:O} \text{C}(\text{C}_6\text{H}_5\text{:O}_2\text{CH}_2)\text{:C}(\text{C}_6\text{H}_3\text{:O}_2\text{CH}_2)$ slender, colourless needles, m. p. 170—171°. H. W.

The Phenanthrene Series. XXXIII. Preparation of Derivatives of Phenanthraquinone and Phenanthrene from 2-Nitrophenanthraquinone. JULIUS SCHMIDT and OTTO SPOHN (*Ber.*, 1922, 55, [B], 1194—1211).—Phenanthraquinone is converted by boiling nitric acid (*d* 1.4) into a mixture of 2-nitrophenanthraquinone, yellow needles, m. p. 258—260°, and 4-nitrophenanthraquinone, m. p. 176—177°, which can be separated by taking advantage of the much smaller solubility of the former in boiling alcohol (cf. Werner, A., 1902, i, 437). 2-Nitrophenanthraquinone is reduced smoothly by Werner's method (*loc. cit.*) to 2-aminophenanthraquinone, dark bluish-violet needles which are not completely molten below 320°; it is characterised by its transformation by *o*-phenylenediamine hydrochloride in boiling aqueous alcoholic solution into 2-aminophenanthraphenazine,



pale yellow needles, m. p. 240° (*hydrochloride*, matted needles, m. p. 298—300°), and by the formation of a *NN*-diacetyl compound, a pale green powder, m. p. 206—208°. 2-Aminophenanthraquinone is converted smoothly into 2-hydroxyphenanthraquinone when it is suspended in concentrated hydrochloric acid and diazotised; subsequently sufficient water is added to give a clear solution, which is heated to its boiling point and then cooled, when the hydroxy-compound separates in almost quantitative yield. The only drawback to the method lies in the relatively very large quantity of water which is necessary. 2-Hydroxyphenanthraquinone is converted by *o*-phenylenediamine hydrochloride into 2-hydroxyphenanthraphenazine, pale brown, microscopic crystals, m. p. 258—259°, and by semicarbazide hydrochloride into the monosemicarbazone, brownish-red crystals, m. p. 263—265° (decomp.).

2-Hydroxyphenanthraquinone is converted by boiling nitric acid (*d* 1.35) into 3:4-dinitro-2-hydroxyphenanthraquinone, a tile-red powder which slowly decomposes above 220°; it cannot be crystallised conveniently, and is best purified by taking advantage of its acidic character, which enables it to dissolve in sodium hydrogen carbonate solution (the sodium salt is described). The presence of the three substituents on the same nucleus is proved by oxidation of the compound by sulphuric acid and potassium dichromate to phthalic acid, whilst the fact that one nitro-group is present in

position 4 is established by the production of 4-aminophenanthrene, m. p. 104—105°, by drastic treatment of the substance with red phosphorus and fuming hydriodic acid (*d* 2.05). The preparation of 3:4-dinitro-2-hydroxyphenanthraquinone, pale brown, microscopic crystals, m. p. 251° (decomp.), of 3:4-dinitro-2-hydroxyphenanthraquinone monoxime, brown crystals, m. p. 211° (decomp.), and of 3:4-dinitro-2-hydroxyphenanthraquinone monosemicarbazone, reddish-brown crystals which do not melt below 270°, is described. Reduction of the nitroquinone with phenylhydrazine and subsequent acetylation of the product gives 3:4-dinitro-2-hydroxyphenanthraquinol diacetate, m. p. 232° (decomp.). 3:4-Dinitro-2-hydroxyphenanthraquinone is reduced by tin and hydrochloric acid to 3:4-diamino-2-hydroxyphenanthraquinone, which is isolated in the form of its hydrochloride. The latter is converted by diazotisation and subsequent boiling with water into 2:3:4-trihydroxyphenanthraquinone, a reddish-brown substance which is completely molten at 235° after incipient decomposition at about 186°. The isolation of the substance is beset with unusual difficulties. It is most definitely characterised by converting it into 2:3:4-trihydroxyphenanthraquinone, dark brown, microscopic crystals, m. p. 255—258° (decomp.), or into its monosemicarbazone, a brownish-red powder which decomposes gradually above 270°.

The bromination of 2-hydroxyphenanthraquinone has been examined, but the process is somewhat inconvenient by reason of the insolubility of the substance in the usual media. The action of bromine on a suspension of the compound in water leads to the formation of a mixture of mono-, di-, and tri-bromo-derivatives, from which only dibromohydroxyphenanthraquinone, reddish-brown crystals, m. p. 255°, could be isolated in an approximately homogeneous condition.

2-Nitrophenanthraquinone is converted by phosphorus pentachloride into a mixture of 9:9-dichloro-2-nitrophenanthrone, yellow needles or leaflets, m. p. 186°, and 10:10-dichloro-2-nitrophenanthrone, pale yellow needles, m. p. 162—163°, which are separated by taking advantage of their widely differing solubilities in benzene. (For the present, the position of the chlorine atoms in the respective compounds is assigned arbitrarily.) The former is reduced by granulated tin and concentrated hydrochloric acid to 2-amino-10-hydroxyphenanthrene, $\text{NH}_2\text{C}_6\text{H}_3\text{C}(\text{OH})\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4$, m. p. 221° (the hydrochloride, dibenzoyl derivative, almost colourless crystals, m. p. 225—226°, and diacetyl compound $[\text{+}\frac{1}{2}(\text{CH}_3\text{CO})_2\text{O}]$, large rhombohedra, m. p. 182°, are described). When treated similarly, 10:10-dichloro-2-nitrophenanthrone yields 2-amino-9-hydroxyphenanthrene, almost colourless, microscopic crystals, m. p. 194—195° (decomp.), the benzoyl derivative of which has m. p. 160° (decomp.). H. W.

Trimethylcamphorylmethylammonium Bromide. H. RITPE (U.S. Pat. 1399082). — Trimethylcamphorylmethylammonium bromide is prepared by heating camphorylbromomethane with an ethereal-alcoholic solution of trimethylamine under pressure for

fifteen hours, cooling, dissolving the desired product (after its precipitation with ether) in chloroform, and reprecipitating it with ether. It forms colourless leaflets, m. p. 192°. On further heating above the m. p., trimethylammonium bromide is separated, which again melts with decomposition at 250°. CHEMICAL ABSTRACTS.

Oxidation of Menthone by Ferric Chloride. YASUHIKO ASAHINA and SABURO MITUORI (*J. Pharm. Soc. Japan*, 1922, 255-263).—By oxidation of menthone with ferric chloride, buchu-camphor is produced. A mixture of 50 grams of menthone, 280 of grams crystallised ferric chloride, and 500 c.c. of 50% acetic acid is gently boiled until the brown colour of the solution is changed to dark green; the oily layer is then separated from the aqueous and distilled with steam, filtered, and the oily filtrate shaken with sodium hydroxide solution. On acidifying, crystals of buchu-camphor separate from the filtrate. Buchu-camphor, after recrystallisation from alcohol, has m. p. 82°, and gives a green coloration with ferric chloride. Attempts to prepare the oxime by the methods of Kondakov and Bjalo-brezeski (A., 1897, i, 227), and Semmler and Mackenzie (A., 1906, i, 373) were unsuccessful. Buchu-camphor reacts, however, easily with phenylcarbimide, forming buchu-camphor phenylurethane, m. p. 113° (Semmler and Mackenzie gave 41°).

When oxidised with potassium permanganate in acetone solution, buchu-camphor gave a syrup, which on cooling changed into white needles, m. p. 129°; from it a semicarbazone, m. p. 217°, was obtained. The product is perhaps identical with Semmler and Mackenzie's diketonic acid. By distilling the crude oxidation product, an unsaturated ketonic acid, m. p. 104—105°, was obtained.

K. K.

Resin Constituents. VIII. The Amyrins from Elemi Resin. II. α -Amyrin. ALOIS ZINKE, ALFRED FRIEDRICH, OTTO JOHANNSEN, and RUDOLF RICHTER (*Monatsh.*, 1921, 42, 439-445; cf. A., 1921, i, 39).—When α -amyrin benzoate is distilled, benzoic acid is split off and a hydrocarbon $C_{28}H_{46}$ $\begin{smallmatrix} <CH \\ | \\ CH \end{smallmatrix}$

is formed. The latter could not be isolated, but forms a crystalline dibromide, $C_{30}H_{48}Br_2$, white, prismatic needles, m. p. 259—260°. The name α -amyrene is proposed for the hydrocarbon, instead of α -amyrien, the name given by Vesterberg (*loc. cit.*) to a probably identical hydrocarbon obtained by the action of phosphorus pentachloride on α -amyrin. Vesterberg's α -amyrene, or, better, α -amyranone, was prepared by oxidation of α -amyrin with chromic acid; it forms crystalline plates or spherical aggregates, m. p. 124°, sintering at 115°. Its oxime, $C_{30}H_{49}ON$, has m. p. 234°. The α -amyranone is very resistant to oxidation and is therefore of little use for elucidating further the structure of α -amyrin. It cannot be obtained in the enol form, but by heating with benzoyl chloride forms a benzoate, α -amyrenol benzoate, $C_{32}H_{50}O_2$, fine leaflets, m. p. 197—198°. Bromo- α -amyrin was oxidised to bromo- α -amyranone, fine, white leaflets, m. p. 190°; its oxime has m. p.

236-5°. *Bromo- α -amyrenol benzoate* crystallises in leaflets, m. p. 226-227°. A loose compound appears to be formed between α - and β -amyrin benzoates, rendering their separation difficult.

E. H. R.

Resin Constituents. IX. The Decomposition of *d*-Siaresinolic Acid and Lubanyl Benzoate. ALOIS ZINKE, FRANZ HANSELMAYER, and WILHELMINE EHMER (*Monatsh.*, 1921, 42, 447-452; cf. A., 1918, i, 398).—By oxidation of *d*-siaresinolic acid in acetic acid solution with Kiliani's mixture (A., 1902, i, 46), and also by oxidising *l*-prabangic acid (A., 1921, i, 331) with potassium permanganate in alkaline solution, a new crystalline acid was obtained, $C_{21}H_{30}O_5$, m. p. 285-286° (decomp.). The acid is dibasic, but neither a crystalline methyl ester nor a hydroxylamine derivative could be obtained.

The formula suggested by Zinke and Drzimal for lubanyl benzoate (A., 1921, i, 187) has been confirmed by fusion with potassium hydroxide, when protocatechuic acid was obtained. The preparation of vanillin from the benzoate afforded further evidence of the correctness of the formula.

E. H. R.

Capsularin, a Glucoside from Jute Leaf. HARIDAS SAHA and KUMUD NATH CHOUDHURY (T., 1922, 121, 1044-1046).

Castelin, a New Glucoside from *Castela Nicholsoni*. LOUIS PIERRE BOSMAN (T., 1922, 121, 969-972).

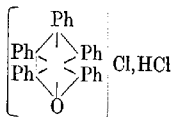
Furfurylidene-1-methylcyclohexan-2-one and some of its Derivatives and the Mono- and Di-furfurylidene-cyclohexanones. (MILE) N. WOLFF (*Compt. rend.*, 1922, 174, 1469-1471; cf. A., 1921, i, 514).—Furfuraldehyde condenses with 1-methylcyclohexan-2-one to give 3-furfurylidene-1-methylcyclohexan-2-one, $C_4OH_3 \cdot CH \cdot C_6H_8 \cdot MeO$, m. p. 51°, R_a 58-30°, R_p 58-96°, R_s 61-21°, which when reduced with sodium amalgam yields 3-furfuryl-1-methylcyclohexan-2-one, $C_4OH_3 \cdot CH_2 \cdot C_6H_8 \cdot MeO$, b. p. 146°/16 mm., R_a 53-60°, R_p 53-92°, R_s 54-82°. The first named compound condenses with magnesium phenyl or *p*-tolyl bromide giving respectively phenylfuryl-2-keto-3-methylcyclohexylmethane, $C_4OH_3 \cdot CHPh \cdot C_6H_8 \cdot MeO$, b. p. 206°/16 mm., R_a 79-03°, R_p 79-39°, R_s 80-70°, and *p*-tolylfuryl-2-keto-3-methylcyclohexylmethane, $C_4OH_3 \cdot CH(C_6H_4Me) \cdot C_6H_8 \cdot MeO$, b. p. 220°/16 mm., R_a 82-96°, R_p 84-52°, R_s 86-61°.

With cyclohexanone, furfuraldehyde gives 1-furfurylidene-cyclohexan-2-one, m. p. 47°, R_a 52-86°, R_p 54-69°, R_s 57-62°, and 1:3-difurfurylidene-cyclohexan-2-one, $C_6H_8O(CH \cdot C_4OH_3)_2$, m. p. 145°, R_a 78-39°, R_p 85-81°, R_s 95-41°.

W. G.

Pyrylium Compounds. XI. Pentaphenylpyrylium Salts. The Formulation of Salts of Dyes. W. DILTHEY [with H. KAFFER] (*Ber.*, 1922, 55, [B], 1275-1279; cf. A., 1921, i, 429).—Benzamarone, $CHBzPh \cdot CHPh \cdot CHPhBz$, is converted by phos-

phorus pentachloride in the presence of boiling chlorobenzene into the 2:3:4:5:6-pentaphenylpyrylium salt (annexed formula), yellow needles, m. p. (indefinite) 248–254°, which does not lose the molecular proportion of hydrogen chloride completely when preserved over time. The nature of the attachment of the chlorine atoms is deduced from the transformation of the hydrochloride into the iron salt, $C_{35}H_{25}OCl_2Fe$, yellow, lustrous needles, m. p. 286–287°, and into the perchlorate, $C_{35}H_{25}O_5Cl$, m. p. 294°. The picrate, $C_{41}H_{27}O_8N_3$, has m. p. 157°. An alcoholic solution of the hydrochloride is converted by sodium carbonate solution at 0° into a mixture of α -diketo- $\alpha\beta\gamma\delta\epsilon$ -pentaphenyl- Δ^2 -pentene, $COPh\cdot CHPh\cdot CPh\cdot CPh\cdot COPh$,



almost colourless needles, m. p. 149–151°, which is readily reconverted into pyrylium salts and tetraphenylfuran, pale yellow leaflets, m. p. 172°.

The communication concludes with a reply to Kehrmann (A., 1921, i, 447) with regard to the relative probability of the formulation of the salts of dyes (cf. Dilthey, A., 1920, i, 324). H. W.

A Synthesis of isoBrazilein and certain Related Anhydro-pyranol Salts. II. Synthesis of isoHæmatein. HERBERT GRACE CRABTREE and ROBERT ROBINSON (T., 1922, 121, 1033–1041).

3:6-Tetramethyldiaminocyanoselenopyronin. M. BATTE-GAY and G. HUGEL (Bull. Soc. chim., 1922, [iv], 31, 440–444).—In proof of the constitution of 3:6-tetramethyldiaminoselenopyronin (cf. A., 1920, i, 629), the corresponding selenoxanthone has been prepared indirectly. If the selenopyronin is oxidised by alkaline permanganate the only product is an amorphous, yellow compound. If, however, the selenopyronin is heated with aqueous potassium cyanide at 65° for ten minutes, a *leucocyanoselenopyronin* is obtained, and if this is oxidised by ferric chloride and hydrochloric acid, 3:6-tetramethyldiaminocyanoselenopyronin, is obtained as its *hydrochloride*, which is readily converted into a crystalline *nitrate*, from which by decomposition with potassium cyanide the free base may be obtained. If the cyanoselenopyronin is warmed with aqueous sodium hydroxide, 3:6-tetramethyldiaminoselenoxanthone, m. p. 261°, is obtained giving coloured salts with concentrated acids which are easily hydrolysed by water.

W. G.

Syntheses in the Benzofuran Group. 6-Methylcoumaran-2-one and 3-Methyl-6-isopropylcoumaran-3-one. I. EFISIO MAMELI (Gazzetta, 1922, 52, i, 322–337).—*o*-Tolyloxyacetic and 3-methyl-6-isopropylphenoxyacetic acid undergo ring-closure when treated with either phosphorus pentachloride or aluminium chloride. The chloride of the original acid represents the first product of the reaction and the new ring is formed by elimination of the chlorine atom and of a nuclear hydrogen atom and is five-membered,

the alkyl substituents of the benzene ring playing no part. The final products are 6-methylcoumaran-2-one and 3-methyl-6-*iso*-propylcoumaran-3-one, respectively.

6-Methylcoumaran-2-one has m. p. 89–90°; the semicarbazone, m. p. 238–240°; oxime, m. p. 152°, and benzylidene derivative, m. p. 111–112° (cf. Stoermer and Bartsch, A., 1901, i, 94; Auwers, A., 1916, i, 496; 1919, i, 216, 217; Higginbotham and Stephen, T., 1920, 117, 1534).

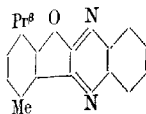
3-Methyl-6-*isopropyl*coumaran-2-one yields the original 3-methyl-6-*isopropyl*phenoxyacetic acid when treated with potassium hypobromite, and treatment of its *isonitroso*-derivative with an acid gives 3-methyl-6-*isopropyl*coumaran-1:2-dione, which forms o-thymotic acid when oxidised by means of hydrogen peroxide and undergoes condensation with *o*-phenylenediamine to 5-methyl-2-*isopropyl*coumarophenazine. In some respects, the heterocyclic ring of 3-methyl-6-*isopropyl*coumaran-2-one behaves differently from those of other coumaranones. Thus, the action of hydrolysing or oxidising agents usually results in opening of the heterocyclic ring by rupture of the linking between the methylene and carbonyl groups, *o*-hydroxybenzoic acids being formed, whereas in the present case this ring resists the action of such agents. Further, the action of hydrochloric acid on oximinocoumaranones mostly effects rupture of the ring between the oxygen atom and the C:OH group and yields *o*-hydroxybenzoylformic acids, but, as stated above, in the present instance the corresponding coumarandione is formed, just as with the oximino-derivatives of acyclic ketones, hydrindones, hydroxythionaphthens, and benzopyrones.

3-Methyl-6-*isopropyl*coumaran-1:2-dione dissolves in cold alkali hydroxide or carbonate solution and is reprecipitable by means of acid. Similar lactonic behaviour is shown by thionaphthaquinone and by β -naphthafuran-1:2-dione and certain dialkylcoumarandiones. As regards the opening of the heterocyclic ring, this dione exhibits behaviour intermediate to that of coumaran-1:2-dione, which is converted into *o*-hydroxybenzoylformic acid by the action of moisture, and that of β -naphthafuran-1:2-dione, which is dissolved slowly by cold and rapidly by hot sodium hydroxide solution. Thus, replacement of the methylene group in the heterocyclic ring of the coumaranone by carbonyl to give the coumarandione causes this ring to open more easily and in a different manner.

6-Methylcoumaranone azine, $C_{18}H_{16}O_2N_2$, prepared by the action of hydrazine hydrate, forms a golden-yellow, crystalline powder, m. p. 223–224°, which begins to darken at 205° and afterwards becomes almost black, and decomposes at 230°.

3-Methyl-6-*isopropyl*coumaran-2-one, $C_{17}H_{14}O_2$, crystallises in long, slender, silky, white needles, m. p. 60°, and gradually becomes oily. It gives a fluorescent solution in alcohol and a greenish-yellow solution in concentrated sulphuric acid, and it decolorises permanganate in presence of sodium carbonate. The oxime, $C_{17}H_{15}O_2N$, crystallises in white scales, m. p. 155–156°; the semicarbazone, $C_{13}H_{17}O_2N_3 \cdot H_2O$, forms a white, crystalline mass, m. p. 191° (decomp.); the benzylidene derivative, $C_{19}H_{18}O_2$,

separates in reddish-yellow needles, m. p. 134°; the *piperonylidene* derivative, $C_{20}H_{18}O_4$, long, deep yellow, silky needles, m. p. 162°; the *oximino*-derivative, $C_{12}H_{13}O_3N$, forms tufts of yellow prisms, or slender needles, or regular rhombic plates, m. p. 164—165°, decomposes at 200°, and yields an *acetyl compound*, $C_{14}H_{15}O_4N$, crystallising in straw-yellow flocks, m. p. 127°.



3-Methyl-6-isopropylcoumaran-1:2-dione, crystallises in bright yellow needles, either interlaced or in stellate aggregates, m. p. 105—106°.

Methylisopropylcoumarophenazine (annexed formula), forms either orange-red or yellow crystals, m. p. 217°, and dissolves in acids, giving yellow salts.

T. H. P.

Syntheses in the Cinchona Series. VII. 5:8-Diaminodihydroquinine and 5:8-Diamino-6-methoxyquinoline and their Conversion into the Corresponding Aminohydroxy- and Dihydroxy-bases. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1922, **44**, 1073—1079).—It has previously been shown that the aminoazo-dyes prepared from 5-aminodihydroquinine and 5-amino-6-methoxyquinoline are easily converted by acids into the corresponding hydroxyazo-dyes (A., 1921, i, 44). This also applies to the 5:8-diamino-derivatives, and there is evidence that the amino-group in position 5 is more labile than that in position 8. Again, it was found that the substitution of a methoxyl group in position 6 is a determining factor as regards the lability of the amino-groups.

8-*p*-Sulphobenzeneazo-5-aminodihydroquinine, on reduction with stannous chloride and hydrochloric acid, gives 5:8-diaminodihydroquinine, an amorphous powder, m. p. 125—140° (decomp.), which is very unstable in light and air and rapidly dissolves in dilute acids, giving red solutions from which crystalline salts can be obtained. The *tetrahydrobromide* and the *basic sulphate* were prepared. Diaminodihydroquinine, when boiled with hydrochloric acid, yielded 5:8-dihydroxydihydroquinine, which is very unstable and is best isolated as its *dihydrochloride*, m. p. 208—211° (decomp.), or its *dihydrobromide*. 8-Amino-5-hydroxydihydroquinine is obtained as its *stannichloride* by the reduction of 5-hydroxy-8-benzeneazodihydroquinine with stannous chloride and hydrochloric acid.

5-Amino-6-methoxyquinoline, when coupled with diazotised sulphanilic acid, yields 8-*p*-sulphobenzeneazo-5-amino-6-methoxyquinoline, from which on reduction with ammonium sulphide 5:8-diamino-6-methoxyquinoline, m. p. 163—164° (decomp.), is obtained. When the latter compound is warmed for thirty minutes on a water-bath with 10% hydrochloric acid, 8-amino-5-hydroxy-6-methoxyquinoline, m. p. 180—182° (decomp.), is obtained, and it may also be prepared from 8-benzeneazo-5-hydroxy-6-methoxyquinoline by the action of ammonium sulphide. 8-*p*-Sulphobenzeneazo-5-amino-6-methoxyquinoline, when heated in acetic acid solution with hydrochloric acid is converted into 8-*p*-sulphobenzene-

azo-5-hydroxy-6-methoxyquinoline, and 5:8-diamino-6-methoxyquinoline, if boiled for three hours with hydrochloric acid, yields 5:8-dihydroxy-6-methoxyquinoline. 5:8-Diaminoquinoline, on the other hand, is recovered unchanged after boiling for three hours with hydrochloric acid.

W. G.

Syntheses in the Cinchona Series. VIII. The Hydrogenation of Dihydrocinchonine, Cinchonine, and Dihydroquinine.

WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1922, **44**, 1079—1090).—Dihydrocinchonine, when reduced with sodium and amyl alcohol, yielded a mixture of hexahydrocinchonine and two epimeric hexahydrodeoxycinchonines, in the last of which the alcohol group as well as the quinoline ring had suffered reduction. The relationship of these compounds to the products obtained by reduction with zinc and hydrochloric acid and by the reduction of cinchonine have been elucidated.

Dihydrocinchonine, when reduced in boiling amyl alcohol with sodium, gave a mixture of bases in the form of an oil, and these were separated by fractional crystallisation of their dihydrochlorides. In this way, the following bases and their derivatives were obtained. α -Hexahydrodeoxycinchonine, m. p. 106—107° (corr.), $[\alpha]_D^{25} +212$ —217°, giving a dihydrochloride, $[\alpha]_D^{25} +69.2^\circ$, a nitroso-derivative as its hydrochloride, m. p. 203—205°, $[\alpha]_D^{25} +68.0^\circ$; an acetyl derivative as its hydrochloride, m. p. 235—237°, $[\alpha]_D^{25} +37.0^\circ$, a benzoyl derivative as its hydrochloride, m. p. 215—220°, $[\alpha]_D^{25} +13.0^\circ$; and 6-benzeneazo- α -hexahydrodeoxycinchonine, m. p. 153—156°. β -Hexahydrodeoxycinchonine, m. p. 106—106.5°, $[\alpha]_D^{25} +18.15^\circ$, giving a dihydrochloride, m. p. 237—240°, $[\alpha]_D^{25} +84.0^\circ$, a nitroso-derivative, m. p. 92.5—93.5° (corr.), $[\alpha]_D^{25} +107.0^\circ$, and its hydrochloride, m. p. 209—211°, $[\alpha]_D^{25} +68.4^\circ$, a benzoyl derivative as its hydrochloride, m. p. 232—234°, $[\alpha]_D^{25} +95.0^\circ$. Hexahydrocinchonine dihydrobromide, $[\alpha]_D^{25} +50.0^\circ$. It is probable that one of the hexahydrodeoxycinchonines described above corresponds with that of Freund and Bredenberg (cf. A., 1915, i, 159), but the hexahydrocinchonine described probably differs from that of Skita and Brunner (cf. A., 1916, i, 835).

Dihydrocinchonine dihydrochloride reacts with phosphorus pentachloride in chloroform solution to give chlorodihydrocinchonine, m. p. 70°, $[\alpha]_D^{25} +36.4^\circ$, and its hydrochloride, m. p. 227—228°, $[\alpha]_D^{25} +48.8^\circ$, which on reduction yields dihydrodeoxycinchonine, m. p. 59.5—60° (corr.), $[\alpha]_D^{25} +113.8^\circ$, and its hydrochloride, m. p. 197—199°, $[\alpha]_D^{25} +69.3^\circ$. Dihydrodeoxycinchonine when reduced with sodium in amyl alcohol gave the two epimeric hexahydrodeoxycinchonines described above.

A repetition of von Norwall's work on the reduction of cinchonine itself by sodium and amyl alcohol (cf. A., 1895, i, 631) resulted in the formation of α -tetrahydrodeoxycinchonine, m. p. 116.5—117.5° (corr.), $[\alpha]_D^{25} +209.0^\circ$, together with a mixture of β -tetrahydrodeoxycinchonine and tetrahydrocinchonine, which were not isolated as such, but were further reduced to the corresponding hexahydro-derivatives.

Dihydroquinine, when reduced in the same manner as the other compounds, yielded mainly *hexahydroquinine*, which could not be isolated as such but as its *dihydrochloride*, m. p. 271—273°, $[\alpha]_D^{25} -36.5^\circ$, as *nitrosohexahydroquinine hydrochloride*, m. p. 212—213°, $[\alpha]_D^{25} -85.1^\circ$, and as *benzoylhexahydroquinine*, m. p. 160—160.5°, $[\alpha]_D^{25} -115.2^\circ$. W. G.

Syntheses in the Cinchona Series. IX. Certain Quinicine and Benzoylcinchona Salts, Crystalline Ethyldihydrocupreine (Optochin) Base, and other Derivatives. MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1922, **44**, 1091—1098).—The following miscellaneous cinchona derivatives, used as initial materials for various investigations, are described. Dihydroquinicine sulphate (cf. Hesse, A., 1888, 69) has m. p. 174—176°, $[\alpha]_D^{25} -8.3^\circ$; *N-methylquinicine dihydrochloride*, m. p. 153—155°, $[\alpha]_D^{25} +16.6^\circ$; *N-methyldihydroquinicine hydrochloride*, m. p. 150—153°, $[\alpha]_D^{25} -9.4^\circ$; *N-ethylquinicine hydrochloride*, m. p. 202—204°, $[\alpha]_D^{25} +68.1^\circ$; *N-ethyldihydroquinicine hydrochloride*, m. p. 202°, $[\alpha]_D^{25} -14.4^\circ$; *N-benzoyldihydroquinicine hydrochloride*, m. p. 161—164°, $[\alpha]_D^{25} -65.9^\circ$; *ethyldihydrocupreicine (optotoxin) sulphate*, m. p. 164—166°, $[\alpha]_D^{25} -7.8^\circ$; *dihydrocupreicine hydrobromide*, m. p. 213—215°, $[\alpha]_D^{25} -5.4^\circ$.

Glycine derivatives of quinicine, described are: *quinicylglycine-anilide dihydrochloride*, m. p. 190°, and *quinicylglycine-p-hydroxy-anilide hydrogen sulphate*, m. p. 212—215°.

The following hydrochlorides of certain benzoylated cinchona alkaloids are described. *Benzoylcinchonidine dihydrochloride*, m. p. 208—211°; *benzoyldihydrocinchonidine hydrochloride*, m. p. 185—190°, $[\alpha]_D^{25} +124.9^\circ$; *benzoylquinine dihydrochloride* (cf. Wunsch, A., 1895, i, 118), m. p. 229—232° (decomp.), $[\alpha]_D^{25} +88.7^\circ$; *benzoyldihydroquinine hydrochloride*, m. p. 235—240° (decomp.), $[\alpha]_D^{25} +140.6^\circ$.

Cinchotenine methyl ester, m. p. 243—244.5° (decomp.), $[\alpha]_D^{25} +118.7^\circ$; *cinchotenine ethyl ester hydrochloride*, and *cupretinine methyl ester dihydrochloride*, m. p. 200°.

Ethyldihydrocupreine (optochin) was obtained in a crystalline form from toluene and had m. p. 123—128°, $[\alpha]_D^{25} -136.2^\circ$. *Ethyldihydrocupreine ethyl bromide* had m. p. 185°, $[\alpha]_D^{25} -111.8^\circ$. *Dihydroquinine ethyl bromide* had m. p. 188—190°, $[\alpha]_D^{25} -111.1^\circ$. *Hydrobromocinchonidine* (cf. Leger, A., 1919, i, 451) had m. p. 176—177° (decomp.), $[\alpha]_D^{25} -226.8^\circ$, and *hydrobromocupreine dihydrobromide* had m. p. 197—203° (decomp.), $[\alpha]_D^{25} -161.8^\circ$. W. G.

Syntheses in the Cinchona Series. X. Dihydrocinchonincol and the Dihydroquinincols. MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1922, **44**, 1098—1107).—It has been found possible to reduce the ketonic group in cinchona alkaloids of the type of cinchonine and quinicine, by means of palladium and hydrogen, the products being mixtures of stereoisomerides of a new type of alkaloids to which the authors have assigned the names dihydrocinchonincols and dihydroquin-

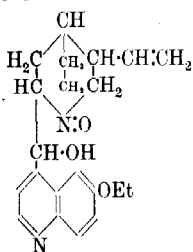
icinols. In general, the *d*-forms proved easier to isolate, and a number of *d*-bases, one of the *l*-bases, and numerous salts of the *d*- and *l*-forms are described. The restoration of the secondary hydroxyl group in the case of the dihydroquinicins resulted in the restoration of the blue fluorescence of the bases when dissolved in excess of nitric or sulphuric acids, thus supporting Kaufmann's statement that the alkyloxy-group and the secondary hydroxyl group are necessary to produce this phenomenon (cf. A., 1913, i, 763, 1222).

From the reduction of cinchonine oxalate *d*-dihydrocinchoninol sulphate, m. p. 223–224°, $[\alpha]_D^{25} + 63.6^\circ$, and the *l*-isomeride, m. p. 232–234°, $[\alpha]_D^{25} - 57.3^\circ$, were obtained.

Derivatives obtained from quinine were *d*-dihydroquininonol nitrate, m. p. 115°, $[\alpha]_D^{25} + 100.7^\circ$; *d*-dihydroquininonol, m. p. 80°, $[\alpha]_D^{25} + 87.1^\circ$; *d*-dihydroquininonol dihydrochloride, m. p. 212–214°, $[\alpha]_D^{25} + 151.8^\circ$ and its *l*-isomeride, m. p. 170°, $[\alpha]_D^{25} - 117.7^\circ$; *d*-*N*-methyldihydroquininonol, m. p. 165.5–166°, $[\alpha]_D^{25} + 93.9^\circ$, and its *d*-hydrobromide, m. p. 218–223°, $[\alpha]_D^{25} + 80.2^\circ$, its *d*-dihydrochloride, m. p. 190°, $[\alpha]_D^{25} + 145.7^\circ$, and its methiodide, m. p. 225–227°, $[\alpha]_D^{25} + 68.7^\circ$; *l*-*N*-methyldihydroquininonol, m. p. 136.5–137.5°, $[\alpha]_D^{25} - 24.9^\circ$, and its dihydrochloride, m. p. 232–235° (decomp.), $[\alpha]_D^{25} + 1.45^\circ$, and its methiodide, m. p. 253–254° (decomp.), $[\alpha]_D^{25} - 50.0^\circ$; *d*-*N*-Ethyldihydroquininonol, m. p. 140–141°, $[\alpha]_D^{25} + 91.7^\circ$, and its hydrochloride, m. p. 135°, $[\alpha]_D^{25} + 85.4^\circ$, its dihydrochloride, m. p. 250° (decomp.), $[\alpha]_D^{25} + 142.6^\circ$, and its methiodide, m. p. 135°, $[\alpha]_D^{25} + 62.9^\circ$. *l*-*N*-Ethyldihydroquininonol dihydrochloride, m. p. 237–238°, $[\alpha]_D^{25} - 16.7^\circ$.

Derivatives obtained from dihydrocupreine were *d*-*O*-ethyl-dihydrocupreicinol, m. p. 105–110°, $[\alpha]_D^{25} + 100.2^\circ$, and its hydrochloride, m. p. 209–210°, $[\alpha]_D^{25} + 81.1^\circ$, and dihydrochloride, m. p. 192–194°, $[\alpha]_D^{25} + 149.2^\circ$. *d*-*N*-Methyl-*O*-ethyldihydrocupreicinol, m. p. 136.5–137°, $[\alpha]_D^{25} + 88.2^\circ$, and *d*-*N*:*O*-diethyldihydrocupreicinol, m. p. 110–111°, $[\alpha]_D^{25} + 87.1^\circ$. W. G.

Action of Hydrogen Peroxide on Cinchona Alkaloids. EDMUND SPEYER and ALFRED GUSTAV BECKER (*Ber.*, 1922, 55, [B], 1321–1329).—Quinine is converted by hydrogen peroxide



hydrocupreine behave in a similar manner, but cinchonine does not appear to yield an amine oxide.

(30%) into an amine oxide which is characterised by its ability to liberate iodine from acidified potassium iodide solution and its re-conversion into quinine by the action of sulphurous acid. Since pyridine and analogous bases do not react with hydrogen peroxide in this manner, it appears valid to conclude that the oxygen atom is attached to the tervalent nitrogen atom of the piperidine complex and to ascribe the annexed formula to quinine oxide. Dihydroquinine, quinidine, dihydrocupreine, and ethyldi-

Quinine oxide, needles, m. p. 185–196°, has $[\alpha]_D -31.44^\circ$ and -29.87° when dissolved in chloroform ($c=2.481$ and 6.207 , respectively). It gives a *dihydrochloride*, leaflets, m. p. 138–140°, a *dinitrate*, colourless rods ($+3H_2O$), m. p. (anhydrous) 152–153° (decomp.), a *normal sulphate*, silky needles, m. p. 146°, after softening at 140°, a *hydrogen sulphate*, needles ($+2H_2O$), m. p. (anhydrous) 165–167°, after becoming pale yellow at 130° and softening at 140°, a *monopicrate*, yellow needles, m. p. 158°, after softening at 156° and a *diperchlorate*, pale brown leaflets, m. p. 193°, after previous softening.

Dihydroquinine oxide is prepared as a yellow liquid by the action of hydrogen peroxide on dihydroquinine or by the catalytic hydrogenation of quinine oxide in the presence of palladium; the *dinitrate* is described.

Quinidine oxide crystallises in coarse octahedra, m. p. 205°; it yields a *picrate*, matted needles, m. p. 152°. *Dihydrocupreine oxide* forms coarse prisms, m. p. 198–202°, after becoming discoloured above 185°. *Ethylidihydrocupreine oxide* crystallises in needles, m. p. 150°, after softening at 135°; its *dinitrate* forms colourless rods, decomp. 153°.

H. W.

The Constitution of Corydaline. J. GADAMER and F. VON BRUCHHAUSEN (*Arch. Pharm.*, 1922, 259, 245–249).—In agreement with the conclusions of Späth and Lang (this vol., i, 168), the

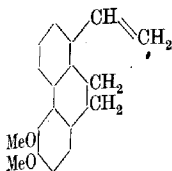
authors now accept for corydaline the formula annexed, since dehydrocorydaline, obtained by the removal of four hydrogen atoms by treatment with mercuric acetate, gives Cannizzaro's reaction when it is warmed with 30% sodium hydroxide solution, 2 mols. being converted thereby by auto-reduction and auto-oxidation into 1 mol. of *oxydehydrocorydaline*, $C_{22}H_{25}O_5N$, m. p. 228–228.5°, and 1 mol. of *dihydrodehydrocorydaline*. This could not occur with the formula previously proposed.

G. F. M.

Ecgonine. J. GADAMER and C. JOHN (*Arch. Pharm.*, 1922, 259, 241–244; cf. this vol., i, 167).—*Anhydroecgonine ethyl ester* is obtained as an oil, b. p. 137–139°/11 mm., $d_{20} 1.0721$, $n_D^{20} 1.49615$; it forms a crystalline *hydrochloride*, m. p. 243–244°. By the action of sulphuric acid, or better chlorosulphonic acid in the cold on *l*-ecgonine the *sulphuric ester* is obtained as a white, crystalline substance, m. p. 258–260°, $[\alpha]_D -85^\circ$; *aurichloride*, $C_9H_{15}O_6NS.HAuCl_4.2H_2O$, m. p. 110° (152–153°, anhydrous). Treatment of anhydroecgonine with cold sulphuric acid did not give the corresponding derivative.

G. F. M.

Morphine. EDMUND SPEYER and GÜNTHER BECKER (*Ber.*, 1922, 55, [B], 1329–1339).—In previous communications (A., 1911, i, 76, 909; 1915, i, 580) the conversion of morphine oxide by acetic anhydride and sulphuric acid into morphinehydrateoxide-



Its methiodide has m. p. 240°. When boiled with sodium hydroxide solution, the methiodide decomposed, giving trimethylamine and dimethoxyvinylidenedihydrophenanthrene (annexed formula), brush-like crystals, m. p. 83·5–84° (corr.). Unlike the known dimethoxyvinylphenanthrene, this dihydro-derivative does not form a picrate. When the methochloride of dimethyldihydroagomorphinethine was reduced with sodium amalgam, it gave, apparently, a mixture of dimethoxyethyl- and -vinylidihydrophenanthenes. Wijn's method of estimating the ethylene linkings by determining the iodine number proved valuable in the analysis of the nitrogen-free products. A number of examples of the application of this method are given.

E. H. R.

E. H. R.

Strychnos Alkaloids. XXXII. Transformations of the Quinones from Brucinesulphonic Acid. I. HERMANN

LEUCHS and KURT FRICKER (*Ber.*, 1922, 55, [B], 1244—1254).—In extension of the work of Leuchs and Geiger (A., 1909, i, 828), the red quinone obtained by the action of 5*N*-nitric acid on brucine-sulphonic acid I has been investigated further. As by-product, a nitro-compound was isolated previously to which the formula $C_{21}H_{23}O_{10}N_3S$ was ascribed; this is now amended to $C_{21}H_{21}O_{10}N_3S$. The substance is shown to be a nitroquinone which is smoothly reduced by sulphur dioxide to a nitroquinol, the formula of which can now be resolved in the following manner:

The red quinone, $C_{21}H_{20}O_7N_2S$, is characterised further by its conversion into a *semicarbazone*, $C_{22}H_{23}O_7N_5S$, pale brown needles, and by reduction with tin and hydrochloric acid to the *aminophenol*, $C_{21}H_{23}O_7N_3S$, short, colourless needles, the *hydrochloride* of which is also described. The quinol, $C_{21}H_{22}O_7N_2S$, gives a *di-acetate*, colourless, slender needles.

The nitroquinone from brucinesulphonic acid I is obtained in the form of a tetrahydrate, yellow, lustrous needles, a *dihydrate*, rectangular or hexagonal prisms, and as the anhydrous compound, $C_{21}H_{21}O_9N_3S$. During its production, the $-CO-N-$ group of brucine and brucinesulphonic acid appears to undergo transformation into the $-CO_2H$ and $NH-$ groups, since it yields an *ethyl* ester, dark yellow, domatic prisms. The quinone group, however, remains intact, since the substance gives a *monosemicarbazone*, yellow leaflets, and a *monoxime*, slender yellow needles, which is almost quantitatively reconverted by warm *N*-nitric acid into the nitroquinone. The oxime is convertible into an *ethyl* ester, dark yellow, rectangular prisms which is transformed by methyl-alcoholic ammonia at 100° into the *methyl* ester of the *nitroquinoneoximeimine*, $C_{22}H_{23}O_9N_3S$, dark yellow needles. Reduction of the nitroquinoneoxime by tin and hydrochloric acid gives the *hydrochloride* of the *diaminophenol*, $C_{21}H_{25}O_9N_3S \cdot HCl$, almost colourless, oblique prisms or plates. Similar reduction of the nitroquinone and treatment of the product

with ethyl alcohol gives the *hydrochloride* of the *amino-quinol* ester, $C_{23}H_{29}O_8N_3S \cdot HCl$, hexagonal plates (the *dihydrate* is also described).

The nitro-quinone is reduced by sulphurous acid at 90° to the corresponding *nitro-quinol*, the *monohydrate*, $C_{21}H_{23}O_{10}N_3S \cdot H_2O$, dark violet, rectangular prisms, the *dihydrate* and *hydrochloride* of which are described; it is readily re-oxidised to the nitro-quinone by 2N-nitric acid or ferric chloride. It yields a *monoethyl* ester, violet leaflets or coarse, blackish-violet, prismatic rods, a *di-ethyl* ester, aggregates of violet leaflets and a *tri-acetyl* derivative, pale yellow, rhombic platelets. The latter is converted by ethyl alcoholic hydrogen chloride into the *ethyl* ester of the *N-monoacetylnitroquinol*, $C_{25}H_{29}O_{11}N_3S$, brownish-yellow leaflets. H. W.

Reduction of Pyridine with Zinc Dust and Acetic Anhydride.
II. OTTO DIMROTH and FRITZ FRISTER (*Ber.*, 1922, 55, [B], 1223—1232; cf. Dimroth and Heene, this vol., i, 48).—In the previous communication it was mentioned incidentally that 1:1'-diacetyltetrahydro-4:4'-dipyridyl, obtained by the reduction of pyridine with zinc dust and acetic anhydride, is frequently contaminated by the presence of an orange-yellow, crystalline compound. This is now shown to be 1:1'-diacetyldihydro-4:4'-dipyridyl. It crystallises in orange-coloured leaflets or needles, m. p. 284° (instead of 248° as previously erroneously reported). The substance is readily oxidised by air to 4:4'-dipyridyl and the process is quantitative when effected with lead tetra-acetate in acetic anhydride solution or by bromine in chloroform (whereby dipyridyl perbromide is produced). The same 1:1'-diacetyldihydro-4:4'-dipyridyl is obtained readily by the reduction of 4:4'-dipyridyl with zinc dust and acetic anhydride. It is very possible that dihydro-4:4'-dipyridyl is the initial product of the reduction of 4:4'-dipyridyl by metals in acid solution but this supposition is not looked on as proved definitely; in any case the authors do not see any reason to suppose with Weitz and Ludwig (this vol., i, 365) that the radicle 4:4'-dipyridinium is present.

The formation of diacetyldihdropyridyl occurs irregularly during the preparation of the corresponding tetrahydro-compound, but the maximum amounts are secured when the mixtures are stirred too long in contact with air at a high temperature. The obvious explanation that the tetrahydro-compound is oxidised by atmospheric oxygen through the dihydro-substance to dipyridyl could not be experimentally confirmed. On the other hand, the dihydro-derivative is produced freely when the tetrahydro-substance is heated with an equivalent amount of dipyridyl in acetic anhydride solution at 100° ; simultaneously, pyridine is formed. It appears therefore that the dihydrodipyridyl is produced entirely by the reduction of dipyridyl and that the tetrahydro-compound is oxidised to pyridine, and not to dihydrodipyridyl.

According to the experimental conditions, oxidation of 1:1'-diacetyltetrahydro-4:4'-dipyridyl leads to the production of dipyridyl or pyridine; the opinion expressed previously (*loc. cit.*)

that this oxidation is preceded by dissociation into radicles is now abandoned.

The peculiar blue coloration which is observed when a solution of diacetyltetrahydrodipyridyl in glacial acetic acid is warmed has been investigated further. It is found that different specimens of the substance give this effect with very varying intensity, and that it is not exhibited by material which has been washed with dilute acetic acid and methyl alcohol immediately before use. It is due to adherent dipyridyl which is formed readily by the autoxidation of diacetyltetrahydrodipyridyl at a rate which is greatly influenced by the presence of catalytic impurities. H. W.

Dialkylamides of Nicotinic Acid. M. HARTMANN and M. SEIBERTH (U.S. Pat. 1403117).—*Nicotinodiethylamide* is prepared by heating nicotiny chloride for two hours at 160° with diethylamine hydrochloride, dissolving the reaction mass in water, adding potassium hydroxide, extracting with ether, and evaporating the ether after drying the solution with an alkali hydroxide. After distillation in a vacuum, it is a yellowish oil, b. p. 280° or 175°/25 mm. *Nicotinodipropylamide* is a yellow oil, b. p. 184°/17 mm. *Nicotinopiperidide* is a thick oil, b. p. 310°.

CHEMICAL ABSTRACTS.

2:4-Diphenylpyridine. C. GASTALDI (*Gazzetta*, 1922, 52, i, 305–307; cf. this vol., i, 573).—2:4-Diphenylpyridine, $C_{17}H_{13}N$, crystallises in elongated, colourless plates, m. p. 69°, exhibits slight basic properties and dissolves in concentrated sulphuric acid to a solution showing faint blue fluorescence. The hydrochloride (2:4-diphenylpyridinium chloride) forms slender, colourless needles and decomposes when heated; the platinichloride, $(C_{17}H_{13}N)_2 \cdot H_2PtCl_6$, crystallises in orange needles with irregular ends, m. p. 238° (decomp.); the picrate, $C_{17}H_{13}N \cdot C_6H_3O_7N_3$, forms thin, yellow plates or stouter prisms, m. p. 187° (decomp.); the methiodide (2:4-diphenyl-1-methylpyridinium iodide), $C_{18}H_{16}NI$, crystallises in very long, yellow needles, m. p. 210° (decomp.), and forms colourless aqueous solutions. T. H. P.

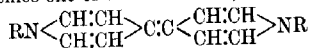
Some Derivatives of Indolinone. OLDŘICH TOMČEK (*Chem. Listy*, 16, 1–4, 35–39).—Brunner's reaction whereby indolinones are prepared from the phenylhydrazides of fatty acids (A., 1896, i, 625; 1897, i, 100, 438; 1898, i, 90), is tried with the phenylhydrazides of β -phenylpropionic acid, and found to give good yields. By its means, a number of benzylindolinones were prepared. Phenylpropionylphenylhydrazine was converted into 3-benzyl-2-indolinone, m. p. 132°. Its 1-acetyl derivative, m. p. 82°, was prepared, also the 5:7-dibromo-derivative, m. p. 194°. 3-Benzyl-1-methyl-2-indolinone, m. p. 95–96°, was prepared by the Brunner reaction from phenylpropionylphenylmethylhydrazine, m. p. 102°, obtained from *as*-phenylmethylhydrazine. 3-Benzyl-7-methyl-2-indolinone, m. p. 196°, was prepared from phenylpropionyl-*o*-tolylhydrazine, m. p. 122°. Its monobromo-derivative has m. p. 191°.

3-Benzyl-5-methyl-2-indolinone, m. p. 149.5°, was prepared from *phenylpropionyl-p-tolylhydrazine*, m. p. 120°. Its *monobromo-derivative*, m. p. 198°, was also obtained. 3-Benzyl-4(or 6)-methyl-2-indolinone, m. p. 209°, was obtained from *phenylpropionyl-m-tolylhydrazine*, m. p. 125°. It was expected that a mixture of the 4- and 6-methyl derivatives would be formed, but only one product was obtained; which of the two it is, it is not yet possible to state with certainty.

R. T.

isoQuinoline and the isoQuinoline-Reds. JOHN EDMUND GUY HARRIS and WILLIAM JACKSON POPE (T., 1922, 121, 1029-1033).

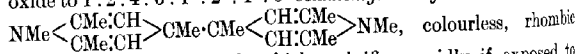
1:1'-Dimethyltetrahydro-4:4'-dicollidyl [1:2:4:6:1':2':4':6'-Octamethyltetrahydro-4:4'-dipyridyl]. BRUNO EMMERT and OTTO WERR (Ber., 1922, 55, [B], 1352-1358).—In a previous communication (A., 1920, i, 331), the blue coloration of alcoholic solutions of 1:1'-dialkyltetrahydro-4:4'-dipyridyls has been attributed to the formation of an alkylpyridinium radicle, $R\cdot NC_5H_4$. The more recent observations of Emmert and Parr (this vol., i, 179) that 4:4'-dipyridyldiisobutyl iodide and 4:4'-dipyridyldiisooamyl iodides in addition to much alkylpyridinium iodide are formed by the action of iodine on the blue solutions of 1:1'-diisobutyl and 1:1'-diisooamyltetrahydro-4:4'-dipyridyls suggests a different interpretation, since one of the substances,



or $RN \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} \text{C} \cdot \text{C} \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} \text{NR}$, must also be present in

the solution; either must be coloured, and, possibly, be the cause of the blue colour of the solutions. To test this point, a dialkyltetrahydrodipyridyl derivative has been prepared in which the labile hydrogen atoms in position 4 are replaced by alkyl groups; this cannot in consequence give such a dialkyldihydrodipyridyl compound. Its alcoholic solution does not become coloured under the action of air or oxygen. The sensitive blue coloration of other dialkyltetrahydrodipyridyls must therefore be attributed to the formation of dialkyldihydrodipyridyls, and it is no longer necessary to assume the rupture of the bond between the pyridine nuclei with the formation of radicles.

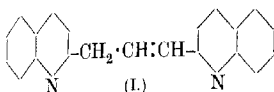
2:4:6-Trimethylpyridine is converted into its methiodide (the *platinichloride* is described) which is reduced by sodium amalgam in aqueous solution and in an atmosphere of carbon dioxide to 1:2:4:6:1':2':4':6'-octamethyltetrahydro-4:4'-dipyridyl,



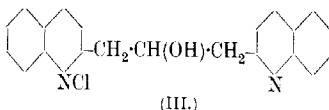
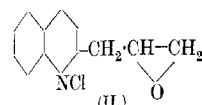
crystals, m. p. 154-155°, which resinifies rapidly if exposed to air, more slowly in an atmosphere of carbon dioxide. An alcoholic solution of the substance decolorises iodine, with the formation of amorphous products in which crystalline material is present in too small quantity to permit further examination.

H. W.

A New Red Quinoline Colouring Matter. M. GIUA (*Gazzetta*, 1922, 52, i, 349—351).—Condensation of quinoline with epichlorohydrin in presence of sodium hydroxide yields an intense dark-red, semi-oily mass which, especially in a desiccator over sulphuric acid, tends to solidify. From the resin thus obtained, alcohol extracts a red compound which dissolves in acids, forms a platinum-chloride, etc., and is probably represented by the annexed formula. The first product of the reaction is most likely the salt-like compound II, which unites with



a second molecule of quinoline under the condensing action of the alkali, giving the compound III, the latter then losing the halogen atom and a molecule of water and undergoing transposition to the compound I:



The red compound, which may be obtained also by condensation of quinoline with α -dichlorohydrin in presence of potassium hydroxide, unites with bromine to give a bromide of high melting point.

The compound (I), $C_{21}H_{16}N_2$, forms a brownish-red solid turning pale yellow in the light, softens at 193° , and is completely fused at 220° ; it dissolves in mineral acids and in acetic acid giving intensely wine-red salts. The *picrate*, $C_{21}H_{16}N_2 \cdot C_6H_3O_3N_3$, forms a brick-red powder; the *platinichloride*, $(C_{21}H_{16}N_2)_2 \cdot H_2PtCl_6$, a dark yellow precipitate dissolving in concentrated hydrochloric acid to a green solution; the *aurichloride*, $C_{21}H_{17}N_2 \cdot HAuCl_4$, a golden-yellow, crystalline powder, and the *nitrate*, $C_{21}H_{17}O_3N_3$, a yellow powder.

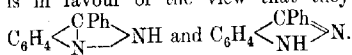
T. H. P.

Bromo-derivatives of Glyoxaline. ISIDORE ELKANAH BALABAN and FRANK LEE PYMAN (*T.*, 1922, 121, 947—958).

Benzylalkylbarbituric Acids. ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1922, 44, 1141—1145).—A series of ethyl benzylalkylmalonates has been prepared either by alkylating the monobenzylmalonic esters or by benzylating the monoalkylmalonic esters. From these ethyl esters the corresponding benzylalkylbarbituric acids have readily been obtained by heating the malonic ester with sodium ethoxide and carbamide in alcoholic solution in an autoclave at 105° for five hours. In this series benzylethylbarbituric acid was found to have the strongest physiological action, but contrary to expectations the hypnotic effect was accompanied by symptoms of tetanus instead of the antispasmodic effect commonly attributed to the benzyl group. New compounds described are: *Ethyl benzylethylmalonate*, b. p. 160 — $170^\circ/9$ mm., *ethyl benzylisopropylmalonate*, b. p. 170 — $180^\circ/12$ mm., *ethyl benzyl-n-butylmalonate*, b. p. 177 — $185^\circ/10$ mm., *ethyl benzylisobutyl-*

malonate, b. p. 177—187°/10 mm., ethyl benzylisoamylmalonate, b. p. 180—190°/10 mm. 5-Benzyl-5-methylbarbituric acid, m. p. 207°, 5-benzyl-5-ethylbarbituric acid, m. p. 206—207°, 5-benzyl-5-n-propylbarbituric acid, m. p. 210°, 5-benzyl-5-n-butylbarbituric acid, m. p. 195°, 5-benzyl-5-isobutylbarbituric acid, m. p. 255°, and 5-benzyl-5-isoamylbarbituric acid, m. p. 194—196°. W. G.

3-Phenylindazole and 2-Hydroxy-3-phenylindazole. K. von AUWERS and K. HÜLTENES (*Ber.*, 1922, 55, [B], 1112—1138).—The recent isolation of stereoisomeric derivatives of 2-acylindazoles (Auwers, A., 1919, i, 455; Auwers and Däesberg, A., 1920, i, 633; Auwers and Schwegler, A., 1920, i, 640), has led to a re-examination of 3-phenylindazole which has been obtained previously (Auwers and Sondheimer, A., 1896, i, 503) in two modifications with different melting points the inter-relationship of which has not been elucidated completely. It is now found that the balance of evidence is in favour of the view that they are structural isomerides,



The new examination of the inter-conversion of the 3-phenylindazoles, m. p. 107—108° and 115—116°, respectively, by recrystallisation or under the action of heat confirms in the main the previous observations (*loc. cit.*), excepting that the changes do not appear to occur with such absolute uniformity as assumed previously. The two modifications give the same hydrochloride and (with acetic anhydride) the same acetyl derivative from which the form, m. p. 107—108°, is obtained by hydrolysis. On the other hand, the phenylindazoles appear to give different picrates which are distinguished from one another in colour, crystalline form, and melting point. The two salts, however, melt indefinitely; on recrystallisation, the melting points approximate to one another without becoming sharp. It appears as if mixtures are formed in every case which tend to pass on crystallisation into a common equilibrium mixture. When triturated with ammonia, the salts give only 3-phenylindazole, m. p. 107—108°.

2-Nitroso-3-phenylindazole, lustrous, greenish-yellow needles, m. p. 91—92°, is prepared readily by the addition of a nitrite solution to 3-phenylindazole dissolved in glacial acetic acid.

The alkylation of indazole leads, according to the experimental condition and the particular alkyl haloid used, to 1- or 2-derivatives or to mixtures of them (Auwers and Schaich, A., 1921, i, 806). Similar relationships are observed with 3-phenylindazole, but, in general, the tendency towards the production of 1-compounds is more marked than with the parent substance. Thus, whereas indazole gives almost exclusively 2-alkyl derivatives when treated with alkyl haloid at 100°, 3-phenylindazole gives, in addition, considerable amounts of the 1-isomerides. Indazole is converted by alkyl haloid and alcoholic alkoxide into about equal quantities of the two isomerides, whereas the main product from 3-phenylindazole is the 1-compound. The difference is not so marked in the case of the action of alkyl iodides on the silver salts, since the

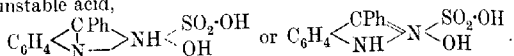
course of the change is here governed mainly by the nature of the alkyl group. The following individual compounds have been examined: 3-phenyl-2-methylindazole, lustrous, apparently monoclinic crystals, m. p. 47—49° (*picrate*, pale yellow needles or granules, m. p. 186—187°); 3-phenyl-1-methylindazole, large, rhombic crystals, m. p. 78.5—80°, b. p. about 207°/12 mm. (*picrate*, very unstable, red crystals, m. p. 91—95°); 3-phenyl-1:2-dimethylindazolium iodide, $C_{15}H_{15}N_2I$, colourless crystals, m. p. 189—190°, which is converted by loss of methyl iodide under the action of heat exclusively into 3-phenyl-1-methylindazole; 3-phenyl-2-ethylindazole, a yellow liquid, b. p. 193—195°/10 mm. (*picrate*, yellow needles, m. p. 160—162°); 3-phenyl-1-ethylindazole, which, unexpectedly, decomposes when distilled in a vacuum (the *picrate* is dark red and very unstable); 3-phenyl-2-allylindazole *picrate*, yellow crystals, m. p. 138—140°; 3-phenyl-1-allylindazole, a yellow liquid, b. p. 215—216°/15 mm. (the corresponding red *picrate* is very unstable).

3-Phenylindazole closely resembles indazole in its behaviour towards chloroformic esters, by which it is smoothly converted into 3-phenylindazole-2-carboxylic esters. The latter are completely hydrolysed by cold alcoholic alkali hydroxide solutions to 3-phenylindazole; at an elevated temperature they lose carbon dioxide, giving 3-phenyl-1- and -2-alkylindazoles and products of further decomposition. Methyl 3-phenylindazole-2-carboxylate forms lustrous, flattened needles, m. p. 112—113°, whilst the corresponding ethyl ester crystallises in colourless needles, m. p. 83—84°.

It has been shown previously (*loc. cit.*) that 2-hydroxy-3-phenylindazole is the main product of the action of sodium sulphite on diazotised *o*-aminobenzophenone, and that the substance is unstable and passes under the prolonged influence of boiling solutions of sodium hydroxide or carbonate into small quantities of benzophenone and nitrogen and a compound, m. p. about 212°. The latter is now shown to be 3-hydroxy-2-phenylindazole, since it is identical with the product obtained by Freundler (A., 1907, i, 158) from hydrazobenzene-*o*-carboxylic acid and phosphoryl chloride (cf. Heller, A., 1917, i, 219). Its constitution is established further by its oxidation by chromic acid in acetic acid solution to azobenzene-*o*-carboxylic acid. Its methyl ether, leaflets with a blue fluorescence, m. p. 95—96°, acetyl derivative, m. p. 90—91°, and benzoyl derivative, colourless, slender needles, m. p. 180—181°, are described. The formation of 3-hydroxy-2-phenylindazole from 2-hydroxy-3-phenylindazole appears to be analogous to the Beckmann transformation, but is regarded as occurring by the direct change in position of the radicals.

Sodium 3-phenylindazole-2-sulphonate, colourless, lustrous leaflets (the corresponding barium, lead, and silver salts are described) is obtained under certain definite experimental conditions, which are fully described in the original, when diazotised *o*-aminobenzophenone is subjected to the action of sodium sulphite. The salt is stable towards boiling water and alkali hydroxide solutions, but is hydrolysed by dilute mineral acids to the salt of 3-phenylindazole and sulphuric acid. It is transformed by the addition of

concentrated hydrochloric acid to its cold concentrated solution into 3-phenylindazole-2-sulphonoxide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CPh} \\ \text{N} \end{smallmatrix} \text{NH} \begin{smallmatrix} \text{SO}_2 \\ \text{O} \end{smallmatrix}$ or $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CPh} \\ \text{NH} \end{smallmatrix} \text{N} \begin{smallmatrix} \text{SO}_2 \\ \text{O} \end{smallmatrix}$, colourless needles, m. p. 195–196°. The substance is insoluble in water or in solutions of alkali hydroxides, is neutral in reaction and is hydrolysed by boiling acids, alkali hydroxides, or even by water, into 3-phenylindazole and sulphuric acid. It is also formed by the action of ethyl chlorosulphonate on 3-phenylindazole or its silver salt. It is remarkable that the alcoholic solution of the sulphonoxide has an acid reaction and liberates carbon dioxide from carbonates. The phenomena are not caused by hydrolysis, and appear to be due to the formation of an unstable acid,



Attempts are also described to prepare sulphonoxides from other indazoles. Sodium 3-methylindazole-2-sulphonate is, however, converted by concentrated hydrochloric acid into the corresponding *sulphonic acid*, m. p. (anhydrous) 185–190°; the *dihydrate*, slender, colourless needles, has m. p. 102–103°, then immediately resolidifies, softens, and evolves gas at 140–156°, and finally melts at 179.5–180.5° (m. p. of 3-methylindazole sulphate). The intermediately evolved gas is sulphur dioxide, due to a subsidiary reaction. Somewhat unexpectedly, 3-methylindazole and indazole are transformed into the corresponding sulphates when mixed with ethyl chlorosulphonate without any special precautions. Possibly the 2-sulphonic acids of the bases are initially formed and subsequently hydrolysed by atmospheric moisture. This hypothesis is supported by the observation that anhydrous 3-methylindazole-2-sulphonic acid is converted into 3-methylindazole sulphate when heated in contact with the atmosphere at 100°, whereas it remains unchanged in the absence of air.

H. W.

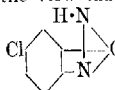
Halogenated Indazoles and Stereoisomerism of Free Indazoles. K. VON AUWERS and H. LANGE (*Ber.*, 1922, 55, [B], 1139–1173).—In extension of previous investigations on the stereoisomerism of 2-acylindazoles (Auwers, A., 1919, i, 455; Auwers and Düesberg, A., 1920, i, 633; Auwers and Schwieger, A., 1920, i, 640), the halogenated indazoles have now been prepared and examined. The first portion of the present communication is devoted to an account of the halogenation of indazoles under varying experimental conditions, and the elucidation of the constitution of the substances so prepared. It is shown that the two rings of indazole are attacked with approximately equal readiness by halogens, which enter it in the 3- and 5-positions. Direct chlorination and bromination yield therefore mainly a 3:5-di-derivative, whereas the preparation of mono-substitution products cannot be achieved in this manner. Monohalogenated indazoles with chlorine, bromine, or iodine in the 3-position are obtained from indazole silver

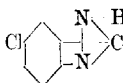
and the respective halogen; probably the halogen atom attaches itself first to the nitrogen, to which the silver was united, and isomerisation subsequently occurs in the established manner. Monohalogenated derivatives with the chlorine or bromine atom in the 5-position are prepared by the action of the halogens on 2-acetyl-indazoles, in which the presence of the acyl group prevents the entry of the halogen atom into the 3-position. Methyl groups attached to one of the two nitrogen atoms attract the halogen to their vicinity and facilitate its entry. 2-Methylindazole thus yields a 3-monobromo-derivative and 1-methylindazole gives a 3:5:7-tribromo-compound, whereas indazole itself only acquires two bromine atoms, even when treated energetically. The chemical nature of indazoles is little affected by the entry of a halogen atom into the benzene nucleus; thus, the 5-halogenated derivatives are somewhat weaker bases than the parent substance, but are readily soluble in 2*N*-hydrochloric acid, combine with picric acid, and are insoluble in solutions of alkali hydroxides. Halogenation in the pyrazole ring, on the other hand, has a powerful influence on the chemical character of the indazoles, the 3-halogenated derivatives dissolving readily in dilute sodium hydroxide solution and being therefore markedly acidic. The degree of acidity diminishes in the order chloro-, bromo- to iodo-derivative. Basic character is little marked in these compounds, since they only dissolve with difficulty even in concentrated hydrochloric acid, and do not give picrates. The behaviour of the 3:5-di-derivatives is somewhat remarkable. As is to be expected, they are very weak bases which are dissolved only with difficulty by concentrated hydrochloric acid and do not give picrates. On the other hand, they appear to be weaker acids than the 3-monohalogenated compounds since they dissolve only in hot solutions of alkali hydroxides from which they separate unchanged on cooling.

The new observations of the stereoisomerism of the 2-acetyl derivatives of indazole completely confirm those made previously (*loc. cit.*). The acetyl compounds of 5-bromo- and 5-iodo-indazoles in addition to the stable forms give labile varieties which, like the corresponding chloro-compounds, are relatively very stable at the atmospheric temperature, but are transformed into the stable modifications slowly at the temperature of the water-bath, rapidly at higher temperatures. On the other hand, it was not found possible to isolate labile acetyl derivatives from 3:5-dichloro-, 3:5-dibromo-, 3-chloro-, or 3-iodo-indazoles. It appears, therefore, that the presence of any substituent in position 3 inhibits the existence of labile 2-acetyl compounds or, at any rate, that such substances are so unstable that they pass immediately into the stable isomerides, even under the mild experimental conditions adopted.

Remarkable observations are recorded with 5-chloro- and 5-bromo-indazoles. The former, m. p. 119–120°, has been obtained by Auwers and Schwegler (*A.*, 1920, i, 642) by the spontaneous decomposition of the nitroso-compound of *p*-chlorobenz-*o*-toluidide. The same substance was obtained also initially by the hydrolysis of the stable acetyl compound of 5-chloroindazole. After a few

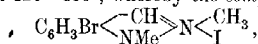
minutes, re-determination of the melting point showed that it had risen to 143—144°, and that this had also occurred with Schwegler's product. A second experiment also yielded 5-chloroindazole, m. p. 119—120° (by hydrolysis of the acetyl derivative), but subsequently the laboratory was found to have become "infected," and only the modification of higher melting point could be isolated. Similar results were obtained with 5-bromoindazole. The substance has been prepared previously by several chemists according to widely differing methods and the melting point 124—125° has been uniformly assigned to it. This is now confirmed. When, however, a specimen was preserved for several weeks the melting point was found to have risen to 132—133°, and subsequently it was not found possible to isolate the variety of lower melting point. The balance of the evidence is in favour of the view that stereo-

isomeric pairs of substances of the type  and

 are here encountered.

The following individual substances are described. 3:5-Dichloroindazole, matted, silky needles, m. p. 240°, prepared by adding chlorine water to indazole dissolved in dilute hydrochloric acid or by passing gaseous chlorine into a solution of indazole in glacial acetic acid; the constitution of the compound is established by its production by the chlorination of 3- or 5-chloroindazole. Its *acetyl* derivative crystallises in slender, colourless needles, m. p. 122—123°. 3-Chloroindazole, m. p. 148° (*acetyl* derivative, m. p. 67°). Stable 5-chloroindazole, colourless, lustrous needles, m. p. 143—144°; the labile and stable modifications give the same *pierate*, m. p. 194—195°. 3:5-Dibromoindazole, m. p. 243—244° (*acetyl* derivative, small, lustrous needles, m. p. 132°). 5-Bromoindazole (labile form, m. p. 124—125°, stable *variety*, m. p. 132—133°; both modifications yield the same *pierate*, m. p. 195—196°). The stable *acetyl* derivative of 5-bromoindazole crystallises in colourless, highly refractive needles, m. p. 143—144°, whereas the labile *modification* (from 5-bromoindazole, silver, and *acetyl* chloride in the presence of anhydrous ether or from 5-bromoindazole and *acetyl* chloride in the presence of pyridine) forms colourless leaflets, m. p. 137—138°; a mixture of the two forms has m. p. 113°. 3-Bromoindazole, m. p. 141—142° (*acetyl* derivative, colourless needles, m. p. 83—84°). 5-Bromo-1-methylindazole, plates or leaflets, m. p. 111—112° (by the action of bromine water on an ice-cold solution of 1-methylindazole in 2*N*-hydrochloric acid). The constitution of the compound is established by methylating 5-bromoindazole in the presence of alkali and transforming the mixture of bases into the corresponding *pierates* which are separated by taking advantage of their differing solubilities in ether. The base obtained by the decomposition of the more readily soluble *pierate* (m. p. 124—126°) is identical with the product just described. 5-Bromo-1-methyl-

indazole is also prepared by heating 3:5-dibromoindazole with methyl iodide at 120—150°, whereby the compound,



m. p. 221° (decomp.), is produced, which when heated above its melting point, loses methyl iodide and gives 5-bromo-1-methylindazole. More drastic bromination of 1-methylindazole leads to the production of mixtures containing a dibromo-derivative, which was not isolated in the pure condition, but in all probability is 3:5-dibromo-1-methylindazole, and 3:5:7-tribromo-1-methylindazole, colourless, lustrous needles, m. p. 168—168.5°. 3-Bromo-2-methylindazole, long, colourless needles or lustrous leaflets, m. p. 82—83°, is prepared by the direct bromination of 2-methylindazole, whereas 5-bromo-2-methylindazole, lustrous needles, m. p. 97—97.5°, cannot be obtained in this manner, but is derived from the methylation of 5-bromoindazole (see above). 3:5-Dibromo-2-methylindazole, lustrous leaflets, m. p. 133—134°, is prepared from 5-bromo-2-methylindazole and an excess of bromine in glacial acetic acid solution. 3-Bromo-5-methylindazole crystallises in soft, matted needles, m. p. 158—159°.

Ethyl indazole-3-carboxylate is converted by acetic anhydride into the corresponding *acetyl* derivative, m. p. 89.5—90.5°, which does not appear to exist in a labile modification.

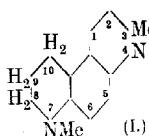
5-Bromoindazole-3-carboxylic acid, pale yellow, matted needles, m. p. 303—305° (decomp.), is obtained readily by the bromination of indazole-3-carboxylic acid dissolved in glacial acetic acid at the atmospheric temperature; its *acetyl* compound crystallises in pale yellow needles, m. p. 220—223°. Ethyl indazole-3-carboxylate is converted by bromine into the compound $\text{C}_{10}\text{H}_9\text{O}_2\text{N}_2\text{Br}_2$, reddish-brown needles, m. p. about 105°, which is converted by a solution of sodium sulphite into *ethyl 5-bromoindazole-3-carboxylate*, m. p. 230—232° (*acetyl* derivative, slender, colourless needles, m. p. 166—167°).

3-Iodoindazole, colourless needles, m. p. 142°, is prepared by the action of iodine on indazole silver in the presence of ether; its *acetyl* derivative crystallises in colourless, lustrous needles, m. p. 93—94°, and does not appear to yield a labile modification. 5-Nitroindazole is reduced by ferrous sulphate and ammonia to 5-aminoindazole, colourless needles, m. p. 170—172°, after previous softening and darkening, which is transformed by successive diazotisation and treatment with potassium iodide into 5-iodoindazole, colourless leaflets, m. p. 157—159°. The corresponding stable *acetyl* derivative (from the iodo-compound and acetic anhydride) forms coarse, yellow crystals, m. p. 144—145°; treatment of 5-iodoindazole with acetyl chloride in the presence of pyridine appears to give a labile *acetyl* compound, which, however, has not yet been isolated in the homogeneous condition. H. W.

The Course of the Quinaldine Synthesis with 6-Amino-tetrahydroquinoline and 6-Aminokairolone. J. LINDNER (*Monatsh.*, 1921, 42, 421—438).—These experiments were started with the object of determining in which direction ring formation

would take place when the quinaldine synthesis was applied to 6-aminotetrahydroquinoline or 6-aminokairolone (6-amino-1-methyl-tetrahydroquinoline), the point having a bearing on the problem of the distribution of double bonds in polynuclear systems. It was found that only the phenanthrene type of derivative was formed, not the anthracene type.

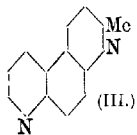
6-Amino-1-methyltetrahydroquinoline was prepared by reduction of 6-nitroso-1-methyltetrahydroquinoline. It has b. p. 163–165°/11 mm., and darkens rapidly in air. The position of the amino-group is inferred from analogy with 6-nitrosotetrahydroquinoline. By the quinaldine synthesis was obtained 3:7-dimethyl-



(I.)

7:8:9:10-tetrahydro-ψ-phenanthroline (annexed formula I). The base crystallises with 1 mol. of water in rhombic four- or six-sided tablets, sulphur-yellow in colour, m. p. 69°. The water is difficult to remove; the anhydrous base has m. p. 52°. The monohydrochloride has an intense red colour, and crystallises in six-sided tablets. The dihydrochloride is colourless. The platinichloride, $C_{14}H_{16}N_2 \cdot H_2PtCl_6 \cdot H_2O$, is a reddish-yellow, crystalline powder, sparingly soluble in water. Demethylation of (I) was accomplished by heating the hydriodide of the base in a stream of carbon dioxide at 160–200°. The demethylated base, 3-methyltetrahydro-ψ-phenanthroline (II), was difficult to purify; its m. p. is probably above 70°. It crystallises with $2\frac{1}{2}H_2O$. Its monohydrochloride is red, and forms a crystalline mass by evaporation of its alcoholic solution; the dihydrochloride is colourless, deliquescent, and difficult to crystallise. By reduction with hydriodic acid and red phosphorus, 3-methyloctahydro-ψ-phenanthroline was obtained. The base could not be crystallised, but the dihydrochloride, $C_{13}H_{18}N_2 \cdot 2HCl$, forms fine, white crystals which sublime without melting. The same octahydro-compound was obtained by reduction of (I), demethylation occurring during reduction. By exhaustive reduction the tetradecahydro-compound was obtained, which was isolated as its platinichloride, $C_{13}H_{24}N_2 \cdot H_2PtCl_6 \cdot H_2O$. By oxidation of the demethylated base (II), with mercuric acetate, four hydrogen atoms were removed, and 3-methyl-ψ-phenanthroline was obtained. It could not be completely purified; the free base had m. p. 98–109°, the tetrahydrate 74–82°.

To confirm the supposed structure of the last compound (annexed formula III), it was prepared by carrying out the quinaldine synthesis on 6-aminoquinoline. The m. p. of the hydrated form ($4H_2O$) was 84–85° and of the anhydrous base 115°. The identity of the two preparations was established thereby proving that the synthesis takes the same course with the 6-amino-1-methyltetrahydroquinoline as with



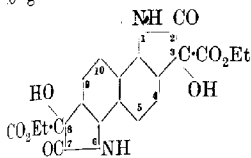
(III.)

6-aminoquinoline.

E. H. R.

A Naphthalenic Di-isatin. JH. MARTINET and F. VACHER
(*Bull. Soc. chim.*, 1922, [iv], 31, 435–440).—1:5-Naphthylene-

diamine condenses with ethyl mesoxalate in acetic acid solution to give ethyl β -naphthabisdioxindole-3 : 8-dicarboxylate (annexed



formula), decomp. about 300° , which gives a diacetyl and a tetraacetyl derivative, both forming colourless crystals. When hydrolysed with aqueous sodium hydroxide in the absence of air and subsequently acidified with hydrochloric acid, the ester yields

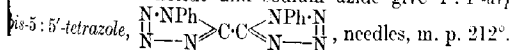
1 : 5-naphthabisdioxindole. If the saponification is carried out in the presence of air with constant agitation, the product is 1 : 5-naphthadi-isatin, which gives a monophenylhydrazine and a diphenylhydrazine. The corresponding sodium and potassium isalates are soluble in water, giving yellow solutions. W. G.

Addition of Hydrazoic Acid to Derivatives of Carbodi-imide. R. STOLLÉ (*Ber.*, 1922, 55, [B]. 1289—1297).—A preliminary description of the preparation of tetrazoles by the action of sodium azide on derivatives of carbodi-imide.

Carbodiphenylimide and carbodi-*p*-tolylimide are converted by sodium azide in boiling absolute alcoholic solution into 5-anilino-1-phenyl-1 : 2 : 3 : 4-tetrazole, m. p. 161° , and 5-*p*-toluidino-1-*p*-tolyl-1 : 2 : 3 : 4-tetrazole, m. p. 211° , respectively. The latter substance is also prepared in good yield by the action of sodium azide and lead oxide on di-*p*-tolylthiocarbimide. By an extension of the method to the corresponding *meta*- and *ortho*-compounds, 5-*m*-toluidino-1-*m*-tolyl-1 : 2 : 3 : 4-tetrazole, coarse leaflets, m. p. 147° , and 5-*o*-toluidino-1-*o*-tolyl-1 : 2 : 3 : 4-tetrazole, needles, m. p. 152° , are obtained. 5-Phenylhydrazin-*o*-1-phenyl-1 : 2 : 3 : 4-tetrazole, from *o*-diphenylthiosemicarbazide, lead oxide, and sodium azide, crystallises in yellowish-white, lustrous leaflets, m. p. 190° (decomp.). Under similar conditions, phenylthiocarbamide yields 5-amino-1-phenyl-1 : 2 : 3 : 4-tetrazole, lustrous leaflets, m. p. 159° , which appears to have been prepared previously from phenylthiocarbimide and hydrazoic acid by Oliveri-Mandalà and Noto (*A.*, 1913, i, 774), who, however, misinterpreted their reaction; it gives an acetyl derivative, small, matted needles, m. p. 211° (decomp.) after previous softening, and a nitroso-compound, decomp. about 108° . 5-Amino-1-*p*-tolyl-1 : 2 : 3 : 4-tetrazole crystallises in colourless, lustrous leaflets, m. p. 176° . Phenylthiocarbimide and *p*-tolylthiocarbimide are converted smoothly by sodium azide in the presence of boiling alcohol into 5-thiol-1-phenyl-1 : 2 : 3 : 4-tetrazole, m. p. 152° , and 5-thiol-1-*o*-tolyl-1 : 2 : 3 : 4-tetrazole, m. p. 131° (decomp.).

Sodium thiocyanate is obtained by the interaction of sodium azide and carbon disulphide in boiling alcoholic solution.

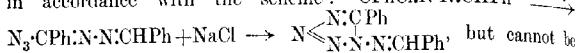
Oxanilideimide chloride and sodium azide give 1 : 1'-diphenyl-



H. W.

bb *2

The Reaction of Benzylidenebenzhydrazide Chloride and Dibenzhydrazide Chloride with Sodium Azide. R. STOLLÉ and A. NETZ (*Ber.*, 1922, **55**, [B], 1297—1305).—Benzylidenebenzhydrazide chloride reacts with sodium azide in boiling ethyl- or methyl-alcoholic solution with the formation of 1-benzylidene-*imino*-5-phenyl-1 : 2 : 3 : 4-tetrazole, m. p. 105° (the corresponding iodochloride, $C_{14}H_{11}N_5ICl$, has m. p. 146°); reaction occurs probably in accordance with the scheme: $CPhCl:N:N'CHPh \xrightarrow{+Na_3N}$



but cannot be arrested at the intermediate stage. With anisylideneanishydrazide chloride in methyl-alcoholic solution it is possible to isolate both *azidoanisylideneanishydrazide*, slender needles, m. p. 113° (decomp.), and 1-anisylideneamino-5-anisyl-1 : 2 : 3 : 4-tetrazole, slender needles or leaflets, m. p. 147°.

Dibenzhydrazide chloride is transformed by sodium azide in boiling methyl-alcoholic solution into *azidodibenzhydrazide*, $N_3 \cdot CPh:N:N'CN_3 \cdot Ph$, long, slender needles, m. p. 139° (decomp.); a sodium salt, $\overset{N:CPh}{N=N} > N \cdot NNa \cdot C \leq \overset{NPh}{N} \cdot \overset{N}{N} \text{ or } \overset{N:CPh}{N=N} > N \cdot N \cdot C \leq \overset{NPh}{N} \cdot \overset{N}{N}$ is formed as by-product. The latter compound is the chief product when boiling ethyl alcohol is used as solvent (in addition, a compound, leaflets, m. p. 172° (decomp.), which is converted by boiling hydrochloric acid into 1-amino-5-phenyl-1 : 2 : 3 : 4-tetrazole); it is also obtained from azidodibenzhydrazide and sodium azide in the presence of boiling ethyl alcohol. The corresponding free acid, $C_{14}H_{11}N_9$, crystallises in small, slender needles, m. p. 192° (decomp.); the silver salt is described. The action of methyl iodide on the silver salt or of methyl sulphate on the sodium compound yields two methyl esters, $C_{15}H_{13}N_9$, short rods, m. p. 150° (decomp.), and coarse crystals, m. p. 124°. The silver salt is transformed by ethyl iodide into two ethyl esters, m. p. 123° and (?) 122°, respectively (mixed m. p. below 120°).

Azidodibenzhydrazide is converted by boiling ethyl alcohol into nitrogen and 1-*azidoethoxymethylamino*-5-phenyl-1 : 2 : 3 : 4-tetrazole, $\overset{N:CPh}{N=N} > N \cdot NH \cdot C(OEt) \cdot NPh$, rhombic plates, m. p. 144° (decomp.) after previous softening. It is transformed by dilute hydrochloric acid into ethyl alcohol, aniline, and 1-amino-5-phenyl-1 : 2 : 3 : 4-tetrazole. 1-*Azidoethoxymethylamino*-5-phenyl-1 : 2 : 3 : 4-tetrazole, rhombic platelets, m. p. 157°, is prepared from the azide and methyl alcohol at 100°.

H. W.

The Replacement of Diazo-groups by Nitro-groups. V. VESELÝ and K. DVOŘÁK (*Bull. Soc. chim.*, 1922, [iv], **31**, 421—424).—For the replacement of the diazo-group by the nitro-group in the Sandmeyer reaction, the authors recommend the addition of a mixture of molecular copper or copper bronze and an alkali nitrite to the solution of the diazonium salt. Such a mixture gives as good a yield as the double copper sulphite and an alkali nitrite. W. G.

Action of certain Hydrazines and of Pyridine on 5-Bromo-1 : 2 : 4-trinitrobenzene. MICHELE GIUA (*Gazzetta*, 1922, 52, i, 346—349; cf. this vol., i, 649).—In the action of hydrazine hydrate on 5-bromo-1 : 2 : 4-trinitrobenzene, the 1-nitro-group is first attacked and eliminated as nitrous acid, so that secondary reactions may occur : (1) $C_6H_2Br(NO_2)_3 + 2N_2H_4 = C_6H_2Br(NO_2)_2 \cdot NH \cdot NH_2 + N_2H_4 + 2H_2O$, (2) $C_6H_2Br(NO_2)_2 \cdot NH \cdot NH_2 + N_2H_4 = C_6H_2(NO_2)_2(NH \cdot NH_2) \cdot N_3 + HBr$, and (3) $C_6H_2Br(NO_2)_3 + 4N_2H_4 = C_6H_2(NO_2)_2(NH \cdot NH_2)_2 + N_2H_4 + 2H_2O + N_2H_4 \cdot HBr$. There exists, therefore, the possibility of the formation of dinitrophenylhydrazinazide, in accordance with equation (2). With excess of hydrazine hydrate, the reaction (3) takes place, whilst with 2 mols. of hydrazine hydrate and 1 mol. of the bromotrinitrobenzene the reaction is represented by equation (1). The action of phenylhydrazine gives rise to 5-bromo-2 : 4-dinitrohydrazobenzene and to 4 : 6-dinitro-1 : 3-dihydrazinobenzene, which decomposes at about 253° (cf. Borsche, A., 1921, i, 461). *as*-Phenylmethylhydrazine yields 5-bromo-2 : 4-dinitromethylhydrazobenzene, and pyridine an additive compound of the type of those obtained by Zincke from 4-chloro-1 : 3-dinitrobenzene and pyridine or quinoline.

5-Bromo-2 : 4-dinitrophenylhydrazine, $C_6H_2Br(NO_2)_2 \cdot NH \cdot NH_2$, crystallises in flattened, lustrous, pale yellow needles, m. p. 203—204°, and gives a yellow coloration with sulphuric acid and a dark red coloration with alkali in presence of alcohol.

5-Bromo-2 : 4-dinitroacetylphenylhydrazine, $C_6H_2Br(NO_2)_2 \cdot NH \cdot NH \cdot Ac$, forms orange-yellow prisms, m. p. 188—189°, and in alcoholic solution gives a dark red coloration with alkali.

5-Bromo-2 : 4-dinitrohydrazobenzene, $C_6H_2Br(NO_2)_2 \cdot NH \cdot NHPh$, crystallises in lustrous, orange-yellow lamellae, m. p. 154—155°, and forms intense reddish-brown salts with alkaline bases.

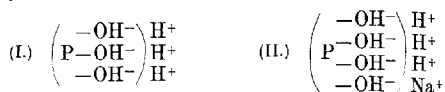
5-Bromo-2 : 4-dinitromethylhydrazobenzene, $C_6H_2Br(NO_2)_2 \cdot NH \cdot NMePh$, forms red prisms, m. p. 138—139°, and in alcoholic solution yields a dark red coloration with alkalis.

2 : 4 : 5-Trinitrophenylpyridinium bromide, $C_5H_5NBr \cdot C_6H_2(NO_2)_3$, crystallises in lustrous, golden-yellow lamellae, m. p. above 300°, and gives a dark red coloration with alkalis. T. H. P.

Colloidal Chemistry of the Proteins. III. A. FODOR (*Kolloid Z.*, 1922, 30, 313—336; cf. A., 1921, i, 81, 701).—From a number of coagulation and peptisation experiments with fibrin sols, together with much previously published data, the author concludes that the dehydration of protein gels leads, exactly as in the case of a large number of inorganic gels, to the formation of new and more stable molecular structures which are characterised by a reduced tendency to enter into reactions, whilst, on the other hand, peptisation of such structure gives, owing to combination with water, reactive disperse particles. It is shown that the larger or smaller particles obtained by precipitating proteins are not to be regarded as accidental, but as structures combined with different

amounts of water and of different reactivity. The author differentiates two stages between the hydrate in which the water is weakly held and the solid swollen gel. These he terms loosely held water (micellar water, and imbibition water) and water adsorbed on the surface. The adsorbed water is regarded as held by the protein owing to it adsorbing one ion of water and giving

a complex which is formulated $(P \leftrightarrow H)OH$ or $(P \leftrightarrow OH)H$. This complex the author terms an "enhydron." In the case of globulin, the enhydron is represented by I; this when treated with alkali becomes through adsorption an alkali enhydron and is represented by II. The character of the enhydron remains unchanged



so long as the adsorbed water is in excess of the alkali, but when the alkali is in excess the complex ceases to be an enhydron and becomes an "ekhydron." In the same way, acid-enhydrons can be formed. The changes of yeast proteins, globulin, and casein are considered on the basis of this hypothesis. J. F. S.

Discrepancies between the Observed and Calculated Potential Difference of Protein Solutions near the Isoelectric Point. JACQUES LOEB (*J. Gen. Physiol.*, 1922, 4, 617-619).—The discrepancies previously noted (A., 1921, i, 627, 693, 822) between the observed values of the influence of the P_H on the potential difference between protein solutions inside collodion bags and protein free aqueous solution and those calculated on the basis of Donnan's theory disappear when both inside and outside solutions contain a buffer salt. This shows that the differences were due to inaccuracies in the measurement of the P_H of the outer solution near the isoelectric point of the protein. C. R. H.

The Regulation of Osmotic Pressure. II. The Effect of Albumin on the Conductivity of a Sodium Chloride Solution. WALTER W. PALMER, DANA W. ATCHLEY, and ROBERT F. LOEB (*J. Gen. Physiol.*, 1922, 4, 585-589).—At a P_H of about 3.0, increasing concentrations of albumin increase the conductivity of 0.6% sodium chloride; at a P_H of 7.3 and at the isoelectric point of albumin, the conductivity is diminished by such additions. C. R. H.

The Proteic Acids of Urine. I. The Hydroxyproteic Acids. S. EULBACHER (*Z. physiol. Chem.*, 1922, 120, 71-84).—The barium salt of hydroxyproteic acid showed the same properties as that described by previous workers. Free hydroxyproteic acid consists of urea, and a carbohydrate, probably a tetrose, which yields an osazone, $C_{16}H_{18}O_6N_4$, m. p. 130°. By treating the substance with alcohol and ether, a compound is obtained which in many respects resembles Moor's urein. Hydroxyproteic acid does

not contain any hexone bases, but possibly traces of other amino-acids. S. S. Z.

The Colloidal Behaviour of Edestin. DAVID J. HITCHCOCK (*J. Gen. Physiol.*, 1922, 4, 597—615).—Edestin reacts like an amphoteric electrolyte and behaves otherwise in a manner entirely analogous to that described by Loeb (A., 1921, i, 627, 693) for gelatin, casein, and albumin. C. R. H.

Kinetics of Trypsin Digestion. JOHN H. NORTROP (*J. Gen. Physiol.*, 1922, 4, 487—509).—Experiments on the rate of hydrolysis of gelatin and casein by trypsin (the rate being measured by the increase of hydrolysis products) show that this rate does not increase in proportion to the substrate concentration, but becomes constant after the latter has reached about 3%. A mixture of casein and gelatin is digested at a rate which is equal to the sum of the rates of hydrolysis of the two substances separately. The rate of digestion is unaffected by the viscosity of the solution or by the concentration of ionised protein. The effect of inhibiting substances on the hydrolysis is independent of substrate concentration, which is taken as evidence against the existence of an enzyme-substrate compound. There is evidence to show that enzyme and inhibitor form a highly dissociated compound. These results may be explained by the fact that the increase of products of hydrolysis does not give a true measure of the change in concentration of substrate. If the decrease of casein or gelatin is measured directly, the reaction is found to conform to the law of mass action, the rate of digestion being proportional to the concentration of substrate. The difference in the results obtained by the two methods is due to the fact that the reaction is not a simple one, but a series of consecutive reactions. C. R. H.

The Digestion of Histone Sulphate with Pepsin and Hydrochloric Acid. K. FELIX (*Z. physiol. Chem.*, 1922, 120, 94—102).—The histone sulphate from the thymus of the calf was digested with pepsin and hydrochloric acid and precipitated with sodium pierate. The filtrate was treated with phosphotungstic acid, and the precipitate again treated with silver baryta. The precipitate from the silver fraction contained a substance resembling the original histone, but the distribution of nitrogen in it was somewhat different, and also it did not give Millon's reaction. The filtrate from the silver fraction showed a content of 17% arginine-N, 13% lysine-N, and 70% monoamino-acid-N. The monoamino-acids of this fraction gave Millon's reaction. The phosphotungstic precipitate showed the presence of peptides, probably dipeptides, but no amino-acids. Lævulinic acid was also found in this fraction, but its origin was traced to the pepsin preparation. S. S. Z.

The Conditions of Acidity and Thermolability of Saccharase. HANS VON EULER and KARL MYRBÄCK (*Z. physiol. Chem.*, 1922, 120, 61—70).—Purified preparations of saccharase manifested the same acidity curve as previously established with

less pure preparations. On the other hand, the purified preparations showed a greater stability towards heat. S. S. Z.

Blood Saccharase and the Antigen Properties of Yeast Saccharase. E. KNAFFL-LENZ (*Z. physiol. Chem.*, 1922, 120, 110—125).—The injection of sucrose into rabbits did not produce a serum capable of inverting this sugar. Immunisation with potent preparations of yeast invertase yielded a serum which inhibited the inverting capacity of invertase only to a small extent. S. S. Z.

Mannanase and Levidulinase. MINORU MAYEDA (*J. Biochem. [Japan]*, 1922, 1, 131—137).—The mannan of the food "konjak-powder" is liquefied by saprophytic bacteria, yielding "levidulin," but not mannose. Certain fungi, such as *Aspergillus niger*, liquefy mannan by their exoenzymes, but also have a distinct endoenzyme which hydrolyses "levidulin." CHEMICAL ABSTRACTS.

Enzymic Fat Synthesis. L. SPIEGEL (*Z. physiol. Chem.*, 1922, 120, 103—109).—On incubating cellulose, dextrose, and starch with enzyme preparations from certain oil-bearing seeds, a low production of fatty substances was established. S. S. Z.

Preparation of Organic Compounds of Boron with the Aid of Boron Fluoride. II. Boron Triphenyl and Phenylboric Acid. ERICH KRAUSE and RUDOLF NITSCHKE (*Ber.*, 1922, 55, [B], 1261—1265; cf. this vol., i, 22).—*Boron triphenyl*, BPh_3 , long, colourless, hexagonal rods, m. p. 136°, b. p. 203°/15 mm., is readily obtained by passing gaseous boron fluoride into an ethereal solution of an excess of magnesium phenyl bromide; it is isolated by distillation of the residue left after removal of the ether, under diminished pressure in an atmosphere of nitrogen. It readily becomes oxidised on exposure to air, without, however, being inflamed; it is stable in an atmosphere of nitrogen or carbon dioxide. It is somewhat rapidly decomposed by alcohol with the formation of esters. If an excess of the Grignard reagent is avoided, the product of the reaction is composed of a mixture of boron triphenyl, *boron diphenyl fluoride*, and *boron phenyl difluoride*; the latter substances have not yet been isolated in a homogeneous condition. Crude boron phenyl difluoride is transformed by hot water into phenylboric acid, $BPh(OH)_2$, which is dehydrated by exposure to phosphoric oxide to phenyl boron oxide, $BPhO$. H. W.

Action of Mercuric Acetate on Nitrobenzene. J. P. WIRAUT and J. JÜRGENS (*Verslag. Akad. Wetensch. Amsterdam*, 1922, 29, 1074—1076).—By heating mercuric acetate with nitrobenzene at 150° for three and a half hours, addition of sodium chloride, and removal of the excess of nitrobenzene by distillation with steam, a light yellow residue is obtained which is separable into *o*-nitrophenylmercuric chloride (Dimroth, A., 1902, i, 656), *mercury oo'-dinitrodiphenyl*, m. p. 206°, and a material insoluble in light petroleum from which a pure substance could not be isolated. CHEMICAL ABSTRACTS.

Mercuriation in the Aromatic Series. I. Phenolmercuri-acetates and -hydroxides and their Derivatives. E. MANEBI (*Gazzetta*, 1922, 52, i, 352—368).—The author has investigated the monomercuri-acetates, -hydroxides, and other salts of phenolmercury obtained from ordinary phenol. Under all experimental conditions, even when a preponderance of phenoldimercuriacetate results, both the ortho- and para-monomercuriacetates are formed. To obtain the monomercuriacetates, it is best to heat the phenol and mercuric acetate together without solvent, whilst in acetic acid solution the product consists almost solely of the dimercuriacetate. In order to determine the positions of the $\cdot\text{Hg}\cdot\text{OAc}$ group in the two monomercuriacetates obtained, these have been converted into the corresponding chlorides, for which the positions of the $\cdot\text{HgCl}$ groups have already been established (Dimroth, A., 1899, i, 54, 428; 1902, i, 656, 849). The action of iodine on *o*-phenolmercuriacetate yields, besides *o*-iodophenol, also 2:4-di-iodophenol and 2:4:6-tri-iodophenol, the reaction being probably catalysed by the mercury compound.

The isomeric phenolmonomercuriacetates have been converted into the corresponding hydroxides, bromides, iodides, nitrates, and sulphates, some of these being obtained by the action of alkali hydroxides or salts on the acetates and others by treating the phenolmercuriooxide with acids. The action of alkali iodides on the acetate sometimes yields the mercuriaryl compound, HgR_2 , which often decomposes, giving the original phenol, but if the reaction is carried out under mild conditions, the phenolmercuriiodide is formed.

Phenol-o-mercuriacetate, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{Hg}\cdot\text{OAc}$, forms long needles or white, dendritic crystals composed of microscopic, hexagonal, or rhombic prisms, and melts at 157° to a turbid, red liquid which afterwards becomes clear and at 210 — 215° decomposes with evolution of gas and red vapour and sublimation of mercury. By alkali hydroxide solution, it is dissolved, with formation of the corresponding hydroxide, and treatment of this alkaline solution with carbon dioxide results in the formation of the internal oxide (Dimroth, A., 1902, i, 849). By hydrogen sulphide, the acetate is not affected in aqueous suspension, but in presence of hydrochloric acid mercuric sulphide is precipitated. In aqueous acetic acid solution, the acetate is converted by sodium chloride into the corresponding chloride.

Phenol-p-mercuriacetate forms long, slender needles or dendritic masses or microscopic, triangular prisms, m. p. 165° , and decomposes at 210 — 215° similarly to the ortho-isomeride.

Phenol-o-mercurichloride has m. p. 156° and the para-compound m. p. 222° (cf. Dimroth, *loc. cit.*).

Phenol-o-mercuribromide, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{HgBr}$, forms slender, silky needles, sometimes in bundles, m. p. 130 — 132° , the clear red liquid becoming turbid at 190° and solidifying and decomposing at 195° . The *mercuri-iodide* crystallises in white, stellar aggregates composed of tufts of short, microscopic prisms, m. p. 121° , the clear red liquid turning turbid at 170 — 180° and decomposing at 200 — 210° . The

nitrate, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{HgNO}_3$, is a white, crystalline, infusible compound, blackening at about 200° . The *sulphate*, $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{Hg})_2\text{SO}_4$, and *hydroxide* are white, pulverulent, and infusible.

Phenol-p-mercuribromide forms scales, m. p. $144^{\text{a}}\text{--}146^\circ$, decomposing and solidifying at $200\text{--}210^\circ$. The *iodide* is obtained as a white powder, m. p. $134\text{--}135^\circ$, and decomposes at $200\text{--}210^\circ$. The *nitrate* forms white crystals and decomposes at 210° . The *sulphate* and the hydroxide are white, infusible compounds. T. H. P.

Mercury Compounds of Hydroxybenzaldehydes. THOMAS ANDERSON HENRY and THOMAS MARVEL SHARP (T., 1922, 121, 1055—1060).

Organo-derivatives of Tin and Lead. I. Application of Lead and Tin Tetraphenyls in the Preparation of Organo-metallic Compounds. ARCHIBALD EDWIN GODDARD, JULIUS NICHOLSON ASHLEY, and RICHARD BROMLEY EVANS (T., 1922, 121, 978—982).

Physiological Chemistry.

Free and Bound Water in the Blood. BENJAMIN S. NETHAUSEN (*J. Biol. Chem.*, 1922, 51, 435—438).—Water imbibed by the serum proteins retains dissolved salts in practically unchanged concentration. Hence it is impossible to prove or disprove theories of bound and free water by physico-chemical methods based on colligative properties. E. S.

The Interactions of Oxygen, Acid, and Carbon Dioxide in Blood. A. V. HULL (*J. Biol. Chem.*, 1922, 51, 359—365).—Mainly a re-statement of the author's theory (this vol., i, 193). E. S.

Active Hyperæmia. D. T. HARRIS (*Proc. Roy. Soc.*, 1922, [B], 93, 384—405).—The increased blood supply to an organ during muscular activity is independent of alterations in vaso-motor or vaso-constrictor tone, but it is due to the products of metabolism. Of these products, carbon dioxide and α -hydroxyacids are found to be increased. C. R. H.

The Distribution of Sugar between Corpuscles and Plasma. W. FALTA and M. RICHTER-QUITTNER (*Biochem. Z.*, 1922, 129, 576—581).—Using exact methods of analysis, corpuscles are found to be free from dextrose if clotting is completely avoided, or if clotting is complete. H. K.

Influence of Optical Activity on Cell Permeability. I. YASUHIRO KOTAKE and M. OKAGAWA (*J. Biochem. [Japan]*, 1922, 1, 159—164).—Colorimetric estimations of *d*-, *l*-, and *dl*-hydroxyphenyl-lactic acid left unabsorbed after incubation with blood

corpuscles in normal saline solution show that only the *l*-compound penetrates the cell-wall to any appreciable extent.

CHEMICAL ABSTRACTS.

Sensitiveness of Cells to Poison as a Function of their Colloid-chemical Conditions. HANS HANDOVSKY (*Kolloid Z.*, 1922, 30, 336—341).—A theoretical paper in which the sensitiveness of cells to poison is discussed in connexion with the colloid-chemical condition of the cells. It is shown that the sensitiveness to poisons and poisoning is of necessity closely connected with the stability and variability of the colloid-chemical condition of the protoplasm colloids. The difference of the sensitiveness of red blood corpuscles to poisoning in solutions of sucrose and in solutions of salts is explained as follows. The sucrose brings about in the continuously changing sol = gel system of the protoplasm a more gelatinised condition, which is accompanied by a decrease in the degree of dispersion, and this makes the blood less sensitive toward the surface active poisons. Solutions of salts act in the opposite sense; they make the blood in sucrose solution sensitive again, and in those cases where the salt has no hæmolytic action of its own it increases the sensitiveness according to the laws which govern the increase in adsorption brought about by the salts. This fact may be regarded as a confirmation of the above quoted hypothesis.

J. F. S.

Glycolytic Action of Leucocytes. I. KANSHI FUKUSHIMA (*J. Biochem. [Japan]*, 1922, 1, 151—158).—The leucocytes, obtained from the peritoneal cavity of rabbits previously injected with bouillon, are suspended in Rona and Michaelis's citrate mixture of p_H 7.765, washed with the aid of a centrifuge, incubated with isotonic glucose solutions for definite periods, and the sugar estimated by Bertrand's method. The reducing power diminishes gradually within forty-eight hours, and then remains constant, but after seventy-two hours it begins to increase again. Neither pancreatic juice nor pancreatic tissue has any effect on the glycolytic action of leucocytes.

CHEMICAL ABSTRACTS.

The Action of the Phosphatides on the Coagulation of Blood. E. ZUNZ and J. LA BARRE (*Arch. int. physiol.*, 1921, 18, 116—127).—A study of the effect of cytozymin, kephalin, and lecithin on blood coagulation in vitro. Cytozymin and lecithin show the solubility characters of the cytozyme of Bordet and Delange (*Ann. inst. Pasteur*, 26, 657, 737). Cytozymin only contains aminated nitrogen; lecithin contains no nitrogen in this form. The addition of small amounts of either of these two compounds to clear serum in the presence of calcium makes such serum induce coagulation in diluted oxalated plasma. An excess of lecithin or cytozymin inhibits coagulation. Cytozyme contains most of its nitrogen in the amino-form. It is probably a mixture of cytozymin and lecithin. Kephalin is to be considered as a thromboplastic agent.

CHEMICAL ABSTRACTS.

Regeneration of Diastase and its Dependence on Oxygen. W. BIEDERMANN (*Biochem. Z.*, 1922, **129**, 582—593).—If an active filtered saliva be heated just to 100°, it becomes turbid. The diastatic activity of this solution is small but is regenerated to a considerable extent by vigorous shaking with air. If, however, the heated saliva be again filtered, the filtrate, free from oxygen, is practically inactive, but is slightly activated by shaking with air. This activation is attributed to oxygen, although the finely divided coagulated protein plays a part. H. K.

Gastric Juice. III. Juice from the Empty Stomach. MAKI TAKATA (*J. Biochem. [Japan]*, 1922, **1**, 107—121).—One hundred c.c. of the juice, *d* 1.006—1.007, yield 1.4873 grams of dry residue, of which 0.5035 gram is ash, and contains pepsin, pepsinogen, rennet, lipase, nuclease, amylase, and maltase, but not sucrase. The mucus content of the juice secreted in unit time does not appear to be influenced either by previous feeding or by the presence of 0.5% hydrochloric acid. The amount of reducing sugar produced by hydrolysis under standard conditions is a measure of the mucus, which exists in the juice in the form of mucoitinsulphuric acid. CHEMICAL ABSTRACTS.

Disappearance of Nitrogen during Digestion. A. GOUIN and P. ANDOUARD (*Bull. soc. hyg.*, 1921, **9**, 381—387).—The digested nitrogen is equal to the dietary nitrogen less the nitrogen of faeces, brushings, hair, etc. In cattle, it is assumed that for each kilo increase in weight, 180 grams of protein containing 28.8 grams of nitrogen are retained as growth-nitrogen, whilst in the case of pigs it is assumed that 19.2 grams of nitrogen are retained for each kilo increase in weight. The results of experiments on calves, adult cattle, and pigs are given. CHEMICAL ABSTRACTS.

The Relative Activities of the Secretins of the Digestive Tract. KATSUMI HARAMAKI (*Biochem. Z.*, 1922, **129**, 503—506).—Experiments on the dog show that all sections of the mucous membrane of the intestines except the jejunum are equally active as regards secretin content. The jejunum is slightly less active. H. K.

Purine Metabolism. Fate of Ingested Purines. MITSUGI KIKUCHI (*J. Biochem. [Japan]*, 1922, **1**, 83—106).—Feeding experiments were carried out for seventeen days with a diet containing only 0.00269 gram of purine-nitrogen; these were followed by three meat periods of six days each with an intake of purine-nitrogen ranging from 0.1—0.3 gram, and finally by three periods of three days each with an intake of purine-nitrogen of 0.22, 0.44, and 0.66 gram respectively. Daily analysis showed that endogenous purine-nitrogen elimination in urine remains about 0.18 gram. Purine-nitrogen in the faeces is about 0.05 gram per day, whether the diet is rich or poor in purine; neither are purine bases in the urine markedly increased on a purine-rich diet. With increase in the intake of purine-nitrogen, its output in the urine likewise increases, but the purine-nitrogen balance shifts con-

tinually. With intakes of 0.00257 to 0.04422 gram of purine-nitrogen, there was a negative balance of -0.1794 to -0.0415 gram per day; with an intake of 0.6623 gram, the balance was $+0.1048$ gram. The amount of purine-nitrogen in urine can be calculated from the formula $Y = (E_0 + aX)(1 + bX)$, where X is the purine-nitrogen intake, Y the amount in the urine, E_0 the endogenous purine-nitrogen, a the kidney coefficient, and b the tissue coefficient. The value of b is usually 0.4 – 0.5 , whilst that of a varies according to the diet, being greater in those living on low purine-nitrogen diets, and is especially small in gouty individuals.

CHEMICAL ABSTRACTS.

Determination of the Carbohydrate Assimilative Power of Man. KOZO SAKAGUCHI, OSAMU ASAKAWA, and TOSHITAKE MATSUYAMA (*J. Biochem. [Japan]*, 1922, **1**, 139–149).—Samples of blood are taken immediately before a test-meal is eaten, and then every half-hour for two hours. Alimentary hyperglycaemia does not exceed 0.14% and the sugar level has returned to the original in one to one and a half hours in normal persons. When the blood sugar rises to 0.15% and hyperglycaemia lasts for two hours, the assimilative power for carbohydrate is impaired.

CHEMICAL ABSTRACTS.

Nutritive Value of Fats and Lipoids. I. KATSUMI TAKAHASHI (*J. Chem. Soc. Japan*, 1922, **43**, 201–242).—The results are summarised as follows: The lipoids, such as cholesterol, lecithin, cephalin, and protagon, or triglycerides have no action like that of fat-soluble vitamin-A; the former have also no action like water-soluble vitamin-B. The lipoids have not only a bad effect on the nutrition of animals, but also a tendency to prevent growth: cholesterol has the worst effect, preventing the growth of young animals and diminishing the resistance to disease. The physiological action of fat-soluble vitamin-A stands in close relation to the metabolism of fats. The greater the molecular weight of a fat, the more fat-soluble vitamin-A is needed. When the quantity of fat is increased, the quantity of fat-soluble-A has to be increased to obtain good nutritive value. Similarly, vegetable fat needs much fat-soluble-A, and fats containing large quantities of sterols have always poor nutritive values in spite of the quantity of vitamin. When triglycerides of different fatty acids are given to animals with food poor in fat-soluble-A, the physiological value of each fat is different. The difference is related to the molecular weights of the fats and is not to be attributed to their relative fusibilities. The nutritive value of fats derived from non-volatile acids decreases with increase in molecular weight, whilst with fats derived from volatile acids the reverse is the case. In general, the nutritive value of fats decreases with diminution of the saponification value; that of fats having a large Reichert-Meissl value is not always bad. When the saponification value is small, the presence of "iodine value" in a fat increases the nutritive value.

K. K.

Phosphatides of Fish Sperm. MINORU SANO (*J. Biochem. [Japan]*, 1922, **1**, 1–16).—Porgy, salmon, and cod sperm were

extracted successively with acetone, ethyl ether, and hot ethyl alcohol, the extracted substances dissolved in chloroform, washed repeatedly with 1% sodium chloride solution, the residue after removal of the chloroform taken up with ether and poured into acetone. The phosphatides thus obtained were free from nitrogenous impurities. The acetone extract contained cholesterol and cholesterol esters; the combined cholesterol formed 7.3% (porgy), 8% (salmon), 4.1% (cod) of the total cholesterol. Lecithin also was present. The fraction insoluble in acetone was chiefly lecithin; one-twentieth to one-thirtieth of the total residue not dissolved by hot ethyl alcohol was probably cephalin and perhaps also sphingomyelin. The portion of the ether extract insoluble in acetone appeared to be curin. The alcohol extract contained (1) cholesterol (80% uncombined) and phosphatides of unknown composition, soluble in cold alcohol and acetone (2) lecithin (from cod) or a mixture of lecithin and cephalin (from salmon), soluble in cold alcohol, but not in acetone. The substance precipitated from the alcoholic extract by cooling consists mainly of cerebrosides; sphingomyelin could also be identified. From 55 to 65% of the total lipid content of fish sperm is phosphatides, 15 to 18% cholesterol, 20 to 30% fats, and 1 to 2% cerebrosides. CHEMICAL ABSTRACTS.

Constitution of the Ovarian Egg of the Carp (*Cyprinus carpio*). E. FAURÉ-FREMIET and (Mlle) H. GARRAULT (*Compt. rend.*, 1922, **174**, 1495—1498).—The ovaries of the carp taken two months before spawning had the following composition: water 66.3%, protein 25.7%, fat 6.2%, cholesterol 0.45%, carbohydrates 0.0%, ash 2.0%. The hyaline globules are constituted by phosphoproteins, and the "ichthidine" by a mixture of a vitellin and a lecithin. The ether extract contains phosphatides 12.33%, glycerides 6.08%, cholesterol 1.34%, unsaponifiable matter 0.8%. W. G.

Fatty Matter in "Herring Roe." KATSUMI TAKAHASHI (*J. Chem. Soc. Japan*, 1922, **43**, 257—268).—Analysis of "Kazunoko," herring roe, gave 8.32% water and 91.68% dried substance; the latter contained total nitrogen 11.22%, fatty matter 14.22%, crude ash 6.03%, and total phosphorus 0.54%. Fat-soluble vitamin-A was present. The fatty matter contained lecithin 48.95%, cephalin 5.62%, cholesterol 7.59%, and oil 37.84%. The oil yielded 24.67% of saturated acids (palmitic and stearic) and 75.13% of unsaturated acids (oleic and other higher acids). The lecithin and cephalin agree in properties and composition with those of the hen's egg. K. K.

Constitution of the Egg of the Trout (*Trutta fario*). E. FAURÉ-FREMIET and (Mlle) H. GARRAULT (*Compt. rend.*, 1922, **174**, 1375—1377).—Ripe trout's eggs at the time of laying contain water 58.5%, protein 29.81%, ether extract 9.16% sugars 0.34%, and ash 1.25%. The vitellin, ichthulin, was isolated and found to contain nitrogen 14.28%, phosphorus 0.57%, and ash 2.17%. The ether extract contained glycerides 10%, phosphatides 8.2%,

at least, and cholesterol 1.37%. The glycerides on hydrolysis yielded oleic and myristic acids. There was a small amount of a reducing sugar, but glycogen could not be detected. W. G.

Optical Properties of Sphingomyelin. MINORU SANO (*J. Biochem. [Japan]*, 1922, 1, 17—20).—Sphingomyelin, prepared from cat's brain, has m. p. 196—198° and contains 3.78% of phosphorus. Its solution in pyridine shows changes in rotatory power with fall of temperature. CHEMICAL ABSTRACTS.

The Liberation of Phosphoric Acid by the Retina in the Presence of Light. HERMANN LANGE and MAX SIMON (*Z. physiol. Chem.*, 1922, 120, 1—29).—The isolated retina of the frog or carp liberates more phosphoric acid in the presence of light than in the dark. In the case of retinae containing pigment epithelium, the liberation of phosphoric acid ceases more quickly when the illumination is stopped than in the case of the isolated neuro-epithelium. When the illumination is renewed the retina with the pigment epithelium shows an increase in the liberation of phosphoric acid. This is not the case when isolated neuro-epithelium is employed. The liberation of phosphoric acid by the isolated pigment epithelium is not influenced by light, and it is found that it contains only small quantities of organic and inorganic phosphorus. It is assumed that the action of the light degrades an organic phosphorus-containing compound with the formation of free phosphoric acid. The latter raises the permeability of the limiting membrane of the retinal epithelium. It is shown that the retina contains a substance which at 45° liberates phosphoric acid rapidly in the presence of sodium hydrogen carbonate. This acidogen which is the source of the phosphoric acid formed by the action of light is not considered to be identical with lactacidogen of transversely striated muscle. S. S. Z.

Oil from the Heads of Sea Animals of the Family Delphinidae. SHŪICHI NAKATOGAWA and SHŪMEI KOBAYASHI (*J. Chem. Ind. Japan*, 1922, 25, 158—168).—The authors have determined the specific gravities, solidifying points, refractive indices, acid, saponification, iodine, Hehner, and Reichert-Wollny values and percentages of unsaponifiable matters (and iodine value of the latter) of oils from the jaw, head, and interior of head of six sea animals belonging to the family *Delphinidae*. [See *J. Soc. Chem. Ind.*, 1922, July.] K. K.

Anticoagulating Substances in the Mucous Membrane of the Uterus. JESSIE L. KING (*Amer. J. Physiol.*, 1921, 57, 44—453).—Pressure juice from the mucous membrane of the non-pregnant uterus of the pig frequently yields antithrombin. The pregnant uterus seldom yields any. Heparin (Howell and Holt, *Amer. J. Physiol.*, 1918, 47, 328) appears to be present sometimes in both the pregnant and non-pregnant pig's uterus, but neither antithrombin nor heparin is obtained with regularity and their presence may be masked by an excess of thromboplastic substance. The presence of fibrinogen, thrombin, and antithrombin

was not demonstrated in menstrual blood. There is reason to believe that it clots as normal blood as it passes the uterine mucosa and that the discharge consists of serum and small particles of clot. There is some evidence that the thrombin of the serum has combined with antithrombin forming metathrombin.

CHEMICAL ABSTRACTS.

The Glycogen of the Embryonic Liver. The Factor determining its Formation. MAX ARON (*Bull. Soc. Chim. Biol.*, 1922, 4, 209—222).—In mammals, the glycogenic function of the liver commences at a period of the foetal life which is constant for the same species, and, in each case investigated, was found to coincide with the appearance of the islets of Langerhans in the pancreas.

E. S.

Action of Hydrochloric Acid on the Fat Exchange in the Surviving Liver. U. LOMBROSO (*Arch. int. physiol.*, 1921, 18, 484—494).—When hydrochloric acid (0.5—1.0%) is given either by the mouth or directly into the duodenum of a fasting dog, and the liver is then isolated and perfused it is found that this organ can destroy fats to a degree equal to or greater than that exhibited by the liver taken from animals during the period of digestion. When the same procedure is carried out on a depancreatised dog no noticeable fat destruction is obtained. These results are interpreted as signifying that the modification of the functional activity of the liver in the fat exchange is not due to an absorption of special products of digestion, but to hydrochloric acid in the duodenum. The pancreas is a necessary factor.

CHEMICAL ABSTRACTS.

The Retention and Distribution of Amino-acids with Especial Reference to the Urea Formation. OTTO FOLIN and HILDING BERGLUND (*J. Biol. Chem.*, 1922, 51, 395—418).—Following a protein meal, the rise in the amino-acid content of the blood precedes that of the urea. The production of urea is not, therefore, a special function of the liver (cf. Van Slyke and Meyer, A., 1914, i, 104). It follows, also, that the excretion of amino-acids is not a test for liver function, although, since the liver is capable of absorbing large quantities of amino-acids, it may serve in cases of cirrhosis as an indication of the extent to which the liver has disappeared.

E. S.

A Basic Peptone-like Substance in the Thymus. K. FELIX (*Z. physiol. Chem.*, 1922, 120, 91—93).—The basic peptone-like substance previously described by the author (this vol., i, 295) gave the following nitrogen distribution according to Kossel and Kutscher's method: total nitrogen in the hydrolysed substance 0.927 gram, arginine nitrogen 0.579 gram, monoamino-acid nitrogen 0.289 gram. No histidine or lysine could be established.

S. S. Z.

Animal Hides as Amphoteric and Colloidal Protein. Theory of Dyeing, Tanning, Disinfection, and Preservation of Leather and the Physiological Action of Tanning Material. M. A. RAKUSIN (*Koll. Chem. Beihefte*, 1922, 15, 103—184).—A paper which is mainly theoretical and in which the author dis-

cusses (1) the theory of the dyeing of animal hides, (2) the tanning of animal hides and gelatin by tannin, (3) the theory of tanning by formaldehyde, aldoses, phenols, picric acid, naphthols, quinone, and "necradol," alum, aluminium, iron, and chromium salts. The part played by water and acid in tanning is discussed and the disinfection and conservation of leather in connexion with the physiological properties of tanning materials are considered. The literature of the subject is considered in connexion with all the above-named points.

J. F. S.

Urea Content of Cow's Milk. Estimation of Urea. YOSHIO MORIMOTO (*J. Biochem. [Japan]*, 1922, **1**, 69—81).—A fairly permanent urease preparation is obtained when 1 gram of finely ground jack-bean is shaken for three hours with a mixture of glycerol and water (8:2) at 40°, 6—7 c.c. of 0.1N-hydrochloric acid are added, the mixture is shaken for one hour, and filtered through paper pulp. Three to five c.c. of urine diluted with 50 c.c. of water, 3 c.c. of urease preparation, and 1 c.c. of indicator (3% calcium caseinate) are incubated for three hours at 38° in a flask closed with a caoutchouc stopper provided with a stoppered funnel, a measured quantity (usually 40 c.c.) of 0.1N-hydrochloric acid is added, and after gentle shaking the excess of acid is titrated with 0.02N-sodium hydroxide solution. Precipitation of casein serves as indicator of the end-point. For the estimation of urea in milk, 10 c.c. are diluted with 40 c.c. of water, 3 c.c. of urease preparation added, and the above procedure carried out. Cow's milk contains 0.025—0.03 gram of urea per 100 c.c., but for a few weeks following calving there is an increase up to a maximum of 0.075 gram, with a rapid fall to normal. Goat's milk contains 0.08 gram of urea per 100 c.c.

CHEMICAL ABSTRACTS.

The Synovial Fluid. F. MALMÉJAC (*Bull. Soc. Chim. Biol.*, 1922, **4**, 190—191).—Results are given of analyses of two different specimens of synovial fluid. Both contained an albumin and an alkali-albumin.

E. S.

Theobromine Excretion and Theobromine Diuresis. LUDWIG GÜNZBERG (*Biochem. Z.*, 1922, **129**, 549—562).—For the estimation of theobromine, the urine is evaporated to dryness with gypsum, extracted with chloroform, and the theobromine removed by precipitation in weakly ammoniacal solution by addition of excess of silver nitrate. The excess of silver is estimated by Volhard's process. Using this method for following the excretion of theobromine in man, a characteristic curve is obtained, showing rapid rise to a maximum after two to three hours and moderately rapid fall. Persons inured to caffeine do not respond so easily to theobromine.

H. K.

Caffeine Excretion in Urine after Tea and Coffee Drinking in Man. KWANICHIRO OKUSHIMA (*Biochem. Z.*, 1922, **129**, 563—569).—The excretion of caffeine after tea and coffee drinking has been followed by Friedberg's method (this vol., i, 88). There is no difference in the excretion after tea or coffee. In the first hour

very little is excreted, more in the second, and most in the third and fourth hours.

H. K.

Composition of the Urine of Whales. S. SCHMIDT-NIELSEN and J. HOLMSEN (*Arch. Int. Physiol.*, 1921, **18**, 128—132).—The urine of five whales was examined and the amounts of the following constituents are tabulated: total nitrogen, urea, uric acid, ammonia, creatinine, protein, ash; potassium, sodium, calcium, and magnesium oxides, chlorine, phosphoric oxide, total sulphur, sulphate, and ethereal sulphates. A relatively large amount of proteinogenous material, partly mucin, was found. Sugar, acetone, and oxalic acid were not found, whilst indican was present. Urobilin tests were positive.

CHEMICAL ABSTRACTS.

Chronic Nephritis with an Unusual Degree of Nitrogen Retention. E. WEISS and V. C. GARNER (*J. Lab. Clin. Med.*, 1922, **7**, 229—232).—The serum of a patient with chronic nephritis had a non-protein nitrogen content of 401 mg. per 100 c.c. twelve hours before death. The urea nitrogen was 304 mg. and the creatinine 13 mg. At an earlier stage when the urea nitrogen of the blood was 246 mg., that of the spinal fluid was 252 mg. At necropsy the following values for tissues and body fluids were found: pericardial effusion 374 mg., muscle 335 mg., liver 332 mg.

CHEMICAL ABSTRACTS.

The Introduction of the Iodine Ion by Electrolysis in a Human Being, and its Elimination by the Urine. GEORGES BOURGUIGNON and CONDUCHÉ (*Compt. rend.*, 1922, **174**, 1437—1440).—Of the iodine introduced into the human system by electrolysis 70—80% is recovered in the urine. During the course of a series of administrations the elimination increases at first for about two days and then remains steady until the administrations are stopped, when it slowly falls and ceases after three or four days. The iodine is better incorporated into the system when introduced electrolytically than when given by the mouth.

W. G.

Toxicity of Neoarsphenamine [Neosalvarsan]. MERRILL C. HART and WILBUR B. PAYNE (*J. Amer. Chem. Soc.*, 1922, **44**, 1150—1160).—The toxicity of commercial samples of neosalvarsan was found to range from 200 to 360 mg. per kilo of body weight for rats. In making such tests, the variability of the test rats is of importance, as it was found that, in some cases, 40—100 mg. difference per kilo was obtained by the same test made on different animals. An apparatus is described for preparing standard solutions of neosalvarsan, and it is suggested that test rats should tolerate doses of 320 mg. per kilo in the form of such a standard solution.

The toxicity of the salvarsan is shown to have a negligible effect on the toxicity of the neosalvarsan prepared from it. The influence of solvents, dilution, time, and temperature on the toxicity of the product as well as the introduction of the methylenesulphinate group and the sulphur distribution have been examined. A curve is given showing the lethal activity of a freshly prepared

solution of neosalvarsan. The introduction of a methylene-sulphinic acid group in the salvarsan increases the tolerated dose of the material from 110 to 320 mg. per kilo (20% of arsenic), but the introduction of the second group was complicated by side reactions giving a higher toxicity.

W. G.

Chemotherapy of Antimony. Comparison of the Antimony Tartrates with the Organic Compounds of Antimony. R. G. FARGHER and WM. H. GRAY (*J. Pharm. Expt. Ther.*, 1921, 18, 341—360).—The following salts of antimony tartaric acid are described: *barium* ($3\text{H}_2\text{O}$), hexagonal plates or flattened prisms; *ammonium* ($1\cdot5\text{H}_2\text{O}$), large flattened prisms; *lithium* ($2\cdot5\text{H}_2\text{O}$), glistening octahedra; *ethylenediamine* (H_2O), flattened prisms, does not melt at 300° ; *butylamine* ($0\cdot75\text{H}_2\text{O}$), hexagonal prisms, m. p. 40° , anhydrous m. p. 155° ; *glyoxaline* ($2\text{H}_2\text{O}$), flattened prisms, does not melt at 300° ; *aniline* (H_2O), elongated, rhombic prisms; *p-phenetidine* (H_2O), felted mass of needles, m. p. 148° , anhydrous m. p. 245° ; *quinine* (H_2O), slender, glistening needles; *quinidine* (H_2O), slender, glistening needles; *cinchonine* ($0\cdot5\text{H}_2\text{O}$), rectangular plates; *cinchonidine* ($2\cdot5\text{H}_2\text{O}$), large, rectangular plates, m. p. 192° ; *hydroquinine* ($5\text{H}_2\text{O}$). The solubility, viscosity, and surface tension of the solution and the minimum lethal dose per kilo of body weight were determined for each salt.

CHEMICAL ABSTRACTS.

The Action of Different Groups of Local Anæsthetics. KONRAD FROMHERZ (*Arch. expt. Path. Pharm.*, 1922, 93, 34—91).—The anæsthetic effects of cocaine, novocaine, various mixed carbonic acid esters, and a substituted ester of β -hydroxybutyric acid were contrasted when the drugs were applied to nerve fibres and directly to nerve-endings (as in the cornea). From the results it was concluded that the group of substances which includes novocaine and the carbonic acid esters, which are easily diffusible, and readily broken down in the body to non-toxic substances, act by means of the nerve-fibres; whereas cocaine and the hydroxybutyric acid ester, which are indeed more toxic but are less readily absorbed, act directly on the nerve-endings and are to be characterised pharmacologically as superficial anæsthetics.

C. R. H.

Caffeine Concentration of the Blood and Urine of Rabbits after Parenteral Administration. L. FARMER LOEB (*Biochem. Z.*, 1922, 129, 570—575).—Intravenously injected caffeine disappears from the rabbit's blood-stream for the most part in a few minutes, the remainder being recognisable for a considerable time during which there is caffeine in the urine and diuresis.

H. K.

Chemistry of Vegetable Physiology and Agriculture.

The Attack of Minerals by Bacteria. Oxidation of Blende. ANDRÉ HELBRONNER and W. RUDOLFS (*Compt. rend.*, 1922, 174, 1378—1380).—Certain bacteria have been found capable of converting blende into zinc sulphate, and the zinc rendered soluble in this manner does not prevent the further action of the bacteria. The oxidation is favoured by the presence of sulphur. These bacteria in the presence of sulphur are capable of producing sufficient sulphuric acid to dissolve the natural silicates and carbonates of zinc. In minerals containing both zinc and lead sulphides, the zinc is converted into soluble sulphate to the exclusion of the lead, and hence this furnishes a means of separating these two metals. W. G.

Physical Chemistry of Alexin-fixation Reaction. JULIUS KISS (*Biochem. Z.*, 1922, 129, 487—502).—The adsorption formula is obeyed by the various forms of alexin fixation, both specific and non-specific. H. K.

Micro-organisms Concerned in the Oxidation of Sulphur in the Soil. III. Media used for the Isolation of Sulphur Bacteria from the Soil. SELMAN A. WAKSMAN (*Soil Sci.*, 1922, 13, 329—336).—The literature concerning the various sulphur-oxidising soil bacteria is reviewed. A classification of the organisms on the basis of their physiological and morphological characteristics is preferred to that adopted by Omelianski. The various media used in the study of the different types of bacteria are detailed. A. G. P.

***Saccharomyces Marxianus* and Top Fermentation Yeast R.** H. VON EULER and K. JOSEPHSON (*Z. physiol. Chem.*, 1922, 120, 42—60).—*Saccharomyces Marxianus* failed to ferment maltose even on the addition of an excess of co-enzyme. It also does not ferment this sugar at a higher temperature, namely, 40°. Its fermenting capacity is diminished on drying, and increases again as the cells imbibe. It ferments sucrose and dextrose with the same velocity. The development of the yeast in dextrose and in maltose solutions is of approximately the same order and follows the ordinary exponential law. Its inverting capacity is about one hundredth of that of culture yeasts. In the case of the top fermentation yeast R both treatment with alcohol and drying diminish its activity. The inverting capacity of yeast R is greater than that of the top fermentation yeast SB. S. Z.

The Energy Yield in the Growth of *Aspergillus niger*. ÉMILE E. TERROINE and RENÉ WURMSER (*Compt. rend.*, 1922, 174, 1435—1437).—The energy yield in the growth of *Aspergillus niger*, after making allowance for the maintenance requirements, is 66–70% of that of the dextrose consumed. W. G.

Formation of Oxalic Acid and Ammonia in Cultures of *Aspergillus niger* on Peptone. WL. BUTKEWITSCH (*Biochem. Z.*, 1922, 129, 445—454).—The proportion of ammonia and oxalic acid formed from cultures of *Aspergillus niger* on peptone corresponds with ammonium oxalate with about 10% excess of ammonia. Of the ammonia formed over a period of ten days, 90% appeared in the first ten days during the vigorous growth of the mould.

H. K.

Utilisation of Peptone as Source of Carbon by *Citromyces* Species. WL. BUTKEWITSCH (*Biochem. Z.*, 1922, 129, 455—463).—*Citromyces glaber* and *C. citricus* grown on peptone media produce ammonia and oxalic acid (not citric acid), the proportion of ammonia being 12 to 20% greater than that required for ammonium oxalate. As in the case of *Aspergillus niger* (previous abstract), the major portion of the ammonia is produced in the first period of growth and the ratio of the yield of mould to ammonia nitrogen falls off with the age of the culture. H. K.

Formation and Accumulation of Oxalic Acid in *Citromyces* Cultures on Salts of Organic Acids. WL. BUTKEWITSCH (*Biochem. Z.*, 1922, 129, 464—476).—Salts of organic acids are utilised by species of *Citromyces* with production of oxalic acid, the sodium salts being more conducive to growth than the ammonium salt. *Aspergillus niger* converts tartaric acid rapidly into oxalic acid; *Citromyces* are unable to do this, but can do so on salts of citric, succinic, and quinic acids with production of considerable quantities of oxalic acid.

H. K.

Action of Selenium, Sulphur, and Tellurium Salts on Plants. BOŽO TURINA (*Biochem. Z.*, 1922, 129, 507—533).—The author has examined the action of selenites, selenates, sulphites, sulphates, tellurites, and tellurates on the germination of plants and on the mature plant. From the deposition of selenium and tellurium by reduction in the tissues, it is concluded that neither selenium nor tellurium salts enter the system in appreciable quantities by way of the root hairs, but that the root-cap plays the important rôle of point of entry and filtration for nutritive salts.

H. K.

Vegetation in Media Poor in Oxygen. L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1922, 174, 1387—1392).—Seeds are not the only organs of a plant which can live for a long time after they have been separated from the plant which produces them. In certain species leaves are capable of preserving their vitality in the absence of air for a relatively long time, which may exceed that required by annual plants to pass through their entire cycle of evolution. It has been shown that small seeds immersed in water may germinate and use up their reserves simply on the small amount of oxygen which aerated water contains.

W. G.

Clay as an Ampholyte. OLOF ARRHENIUS (*J. Amer. Chem. Soc.*, 1922, 44, 521—524).—It is shown that clays of different origin

and different reaction have the same isoelectric point and the curve obtained by plotting the rate of settling against the hydrogen-ion concentration has the same course as that of gelatin. The clay acts as an amphoteric electrolyte and can therefore combine with either acid or base. This is also shown by the buffer action of clays.

J. F. S.

The Effect of Drying Soils on the Water-soluble Constituents. A. F. GUSTAFSON (*Soil Sci.*, 1922, **13**, 173—213).—Comparison is made of the water extracts of a number of soils dried in air, in an oven, and in an autoclave. In general, drying increased the amount of water-soluble material in the soils, but heating above 100° caused a loss in nitrates. Storage of soils at the ordinary temperature for nine weeks had little effect on the quantity of soluble constituents provided the moisture content was maintained, but kept below saturation point. In view of the results obtained, it is noted that in pot culture work it is highly important that soils should be kept under strictly comparable conditions of moisture, temperature, and aeration.

A. G. P.

Relation of Hydrogen-ion Concentration in Soils to their "Lime Requirement." HARLAN W. JOHNSON (*Soil Sci.*, 1922, **13**, 7—22).—In the great majority of soils there appears to be no relation between the lime requirement as estimated by the Veitch method (A., 1903, ii, 400) and the hydrogen-ion concentration; the Truog method (A., 1916, ii, 404), however, yields results which are a combination of the Veitch lime requirement and the hydrogen-ion concentration. In soils of similar type, there is a relation between the apparent quantity of acids and the strength of the acids. Acidity in mineral soils appears to be due to weathering and leaching rather than to accumulation of organic acids, and clay particles and organic substances act as "buffers" to lower the hydrogen-ion concentration.

W. P. S.

Origin of Soil Colloids. MILTON WHITNEY (*Science*, 1921, **54**, 653—656).—Microscopical examination during the mechanical analysis of soil shows that the clay particles range in diameter from 0.005 to 0.0001 mm. It is assumed that towards the lower limit of size, the particles contain relatively few molecules, and that the bombardment of the water molecules in which the particle is immersed causes disintegration. The atoms of calcium, magnesium, potassium, and sodium in the molecule of the silicate would go for the most part into true solution, whilst the atoms of silicon, aluminium, and iron would go chiefly into colloidal solution, forming the basis of the colloidal matter or ultra clay of the soil. The only known means of changing the colloidal nature of the absorptive soil colloids is to heat the material at 1000° in order to secure complete dehydration.

A. A. E.

Organic Chemistry.

Catalytic Transformation of Vegetable and Animal Oils into Petrol. ALPHONSE MAILHE (*Ann. Chim.*, 1922, [ix], **17**, 304—332).—A more detailed account of work already published (*A.*, 1921, i, 706, 841; this vol., i, 424). W. G.

The Catalytic Oxidation of Saturated Paraffin Hydrocarbons and Fatty Acids. ARTHUR HENRY SALWAY and PERCY NOEL WILLIAMS (*T.*, 1922, **121**, 1343—1348).

Densities and Refractive Indices at 15° of Mixtures of Water, Alcohol, and Ether. A. SANFOURCHE and A. M. BOUTIN (*Bull. Soc. chim.*, 1922, [iv], **31**, 546—551).—The densities and refractive indices at 15° of a large number of mixtures of water, ethyl alcohol, and ethyl ether in varying proportions are tabulated, and the results are also shown in triangular diagrams. W. G.

Catalysis. II. Dehydration and Addition Reactions of Ethyl Alcohol: the Formation of Acetal and Mercaptans. FRANÇOIS A. GILFILLAN (*J. Amer. Chem. Soc.*, 1922, **44**, 1323—1333; cf. *A.*, 1921, i, 806).—A comparison of the activity of the oxides of silicon, thorium, titanium, and tungsten in inducing certain catalytic dehydration and esterification reactions with ethyl alcohol vapour.

Ethyl alcohol vapour, alone or in the presence of carbon dioxide, is not decomposed when passed over pumice even at 500°. Thorium oxide is not exclusively a dehydrating catalyst, as, under certain conditions, a considerable amount of acetaldehyde is produced by dehydrogenation. In the presence of carbon dioxide, a quantity of acetal is obtained from the alcohol. The oxide is inactivated for dehydration of the alcohol if it is strongly calcined or heated for a long time at a lower temperature before use. Up to about 340°, the blue oxide of tungsten is a more effective dehydrating agent for ethyl alcohol than is thorium oxide, but above this temperature the two oxides are practically of equal efficiency. Titanium oxide has no dehydrating action up to 355°. In no case was any ether produced from the alcohol.

In the presence of any of the three metallic oxides as catalysts at 300—400° a mixture of absolute alcohol and carbon disulphide produced considerable quantities of ethyl mercaptan, titanium oxide being the most active catalyst for this reaction. At the same time, small amounts of unidentified liquids with high boiling points were obtained.

Pure, dry carbon disulphide, when vaporised over pumice or the

blue oxide of tungsten, was not decomposed at temperatures up to 400°, but in the presence of a trace of moisture hydrogen sulphide was obtained.

W. G.

The Preparation of Dialkylvinylcarbinols. R. LOCQUIN and SUNG WOUSENG (*Compt. rend.*, 1922, **174**, 1551—1553).—Dialkyl-ethinylcarbinols of the type $\text{HO-CRR}'\text{-C}\equiv\text{CH}$ (this vol., i, 617), when hydrogenated in the presence of reduced nickel under controlled conditions, give dialkylvinylcarbinols, $\text{HO-CRR}'\text{-CH:CH}_2$, which have a great tendency to retain water, with which they form more or less stable hydrates. These new carbinols are easily dehydrated, giving hydrocarbons, and they react with magnesium methyl iodide, giving a theoretical evolution of methane. They are not converted into esters under normal conditions, but they give crystalline allophanates. The compounds described are, *methylisohexylvinylcarbinol*, b. p. 89—91°/15 mm.; *dipropylvinylcarbinol*, b. p. 75—76°/12 mm., and its *allophanate*, m. p. 112°, and *methyl-ψ-butylvinylcarbinol*, b. p. 146—147°, d_4^{20} 0.8576, n_D^{20} 1.4432, and its *allophanate*, m. p. 167—168° (decomp.). W. G.

Δ^α-Butene-γ-ol. [α-Methylallyl Alcohol]. J. BAUDREX-GHIEN (*Bull. Soc. chim. Belg.*, 1922, **31**, 160—170; cf. Wohl and Losanitsch, A., 1908, i, 934).—If this alcohol is prepared from distilled acetaldehyde which has been stabilised with quinol (Moreu, Dufraisse, Robin, and Pougnet, A., 1920, i, 144), the yield is increased from 25% to 52%. The pure alcohol has d_4^{20} 0.8318, n_D^{20} 1.412746, $n_{H_2O}^{20}$ 1.40944, $n_{H_2O}^{25}$ 1.41848, n_D^{25} 1.42385. The measurement of viscosity of mixtures of α-methylallyl alcohol and water show that a maximum figure is reached for a mixture corresponding with the hydrate $\text{OH}\cdot\text{CHMe}\cdot\text{CH:CH}_2\cdot 4\text{H}_2\text{O}$. The haloid esters are easily transformed into their isomerides so that the series of transformations $\text{OH}\cdot\text{CHMe}\cdot\text{CH:CH}_2 \xrightarrow{\text{HCl}} \text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\text{Cl} \xrightarrow{\text{KOAc}} \text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OAc} \xrightarrow{\text{KOH}} \text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ can be carried out; the series may be reversed, but the yields obtained are smaller. It is pointed out that this reverse series is more frequently met with in the case of these haloid esters. The following substances have been prepared: γ-chloro-Δ^α-butylene, b. p. 64°/766 mm., d_4^{20} 0.8978, n_D^{20} 1.41493; α-chloro-Δ^β-butylene, b. p. 84°/766 mm., d_4^{20} 0.9282, n_D^{20} 1.43503; α-bromo-Δ^β-butylene, b. p. 104—107°, d_4^{20} 1.333, n_D^{20} 1.47716, γ-acetyl-Δ^α-butylene, b. p. 111—112°/752 mm., d_4^{20} 0.90235, n_D^{20} 1.40386; α-acetyl-Δ^β-butylene, b. p. 132.5—133.5°/752 mm., d_4^{20} 0.91915, n_D^{20} 1.41806; α-chloro-β-bromobutane, b. p. 146—147°/755 mm., d_4^{20} 1.468, n_D^{20} 1.4800. H. J. E.

Transformation of Tertiary Ethylenic Alcohols (Linalol Type) into Primary Ethylenic Alcohols (Geraniol Type). R. LOCQUIN and SUNG WOUSENG (*Compt. rend.*, 1922, **174**, 1711—1713).—Dialkylvinylcarbinols of the type $\text{HO-CRR}'\text{-CH:CH}_2$ readily undergo isomerisation when heated with glacial acetic acid at 110—115° for fifteen hours, giving γγ-dialkylallyl alcohols

of the type $\text{CRR}'\text{CH}\cdot\text{CH}_2\cdot\text{OH}$, which by controlled oxidation give the corresponding $\beta\beta$ -dialkylacetaldehydes and on further oxidation the ketones, CORR' . Thus methylisohexylvinylcarbinol gives γ -methyl- γ -isohexylalyl alcohol, b. p. $110^\circ/12$ mm., yielding on oxidation β -methyl- β -isohexylacetaldehyde, b. p. $95-105^\circ/12$ mm., giving a semicarbazone, m. p. 164° . Dipropylvinylcarbinol yields γ -dipropylalyl alcohol, b. p. $99-101^\circ/12$ mm., giving an allophanate, m. p. $147-148^\circ$, and on oxidation $\beta\beta$ -dipropylacetaldehyde, which gives the semicarbazone, m. p. $171-173^\circ$. Methyltert.-butylvinylcarbinol yields γ -methyl- γ -tert.-butylalyl alcohol, b. p. $84^\circ/12$ mm., and its allophanate, m. p. 77° . β -Methyl- β -tert.-butylacetaldehyde, b. p. $75-78^\circ/15$ mm., gives a semicarbazone, m. p. $204-205^\circ$, and on oxidation β -methyl- β -tert.-butylacrylic acid, m. p. 85° .
W. G.

Composition of the Residue on Distillation of Crude Glycerol. ARCHIBALD RAYNER (*J. Soc. Chem. Ind.*, 1922, **41**, 224-225r).—A criticism of a paper by Lewis on the above subject (this vol., i, 419). The author considers that the organic impurities in glycerol residues generally amount to 40% of the inorganic salts, and not to only 7% as stated, and that no polyglycerols are present in commercial crude glycerol, even when made by the autoclave process. The composition of the residues cannot be estimated in terms of glycerol and diglycerol from determinations of their hydroxyl value, as not only are other hydroxy-compounds present, but some of the polymerisation products are of the glycide type with low hydroxyl values, or possibly no hydroxyl value at all. Of this class of compounds the glycides of glycerol, diglycerol, and triglycerol are known. They are liquids of low viscosity and lower boiling points than the parent glycerols. Attempted polymerisation of glycerol by 0.05% of iodine failed to give an 85% yield as stated, very little polymerisation at all being obtained under the conditions described. G. F. M.

Physico-chemical Properties of Phospholipin. I. Precipitation of Lecithin Hydrosol by Electrolytes. SAMURO KAKIUCHI. (*J. Biochem. [Japan]*, 1922, **1**, 165-174).—Lecithin particles have a negative charge in aqueous solution. Addition of salts with univalent cations does not cause precipitation, but salts with bi- or ter-valent cations cause precipitation within a certain range of their concentration. The range of precipitation concentrations is broad in the former case, but narrow in the latter case, and in the former a greater concentration is required. Contrary to Hardy and Schulze's law, the ion of an electrolyte of similar charge to the colloid has an effect on the precipitation of the colloid, this becoming more marked when the valency of the similarly charged ion becomes higher. Further, the validity of antagonistic action between uni- and bi-valent cations is questioned; it is maintained that the antagonism is between anions and cations.

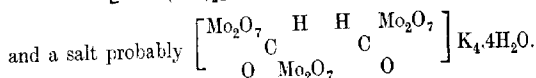
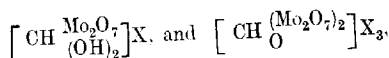
CHEMICAL ABSTRACTS.

Triethylene Tri- and Tetra-sulphides. II. SIR PRAFULLA CHANDRA RÂY (T., 1922, **121**, 1279—1283).

Preparation of Anhydrous Formic Acid. M. C. BOSWELL and H. E. CORMAN (*Can. Chem. Met.*, 1922, **6**, 63—65).—When molar proportions of sodium formate and 100% sulphuric acid are mixed, allowed to remain for seventeen hours, and then distilled on a water-bath under 15–20 mm. pressure, an 85% yield of 95% formic acid is obtained, whereas by distillation at atmospheric pressure only a 25% yield of 90% formic acid is obtained. Distillation of a mixture of sodium formate and sodium hydrogen sulphate (D.R.-P. 209418) gives a 56% yield of 82.7% formic acid. Fractional crystallisation, in a freezing mixture, of 88% acid yields crystals of 95% acid, whilst from 97% acid, crystals of 99.6% purity can be obtained.

CHEMICAL ABSTRACTS.

Researches on the Photochemically Sensitive Compounds of Molybdic and Formic Acids. W. F. JAKÓB (*Roczniki Chemii*, 1921, **1**, 411—423).—The salts of molybdeno-orthoformic acids are prepared and investigated. From six possible types of acids, the author succeeds in preparing only the sodium, potassium, and ammonium salts of the types:



All the salts prepared are photochemically sensitive, becoming green, yellow, or brown on exposure to light. They are obtained as crystalline precipitates from solutions of the respective molybdates, strongly acidified with formic acid. They cannot be recrystallised, as they decompose in solution.

R. T.

Catalytic Decomposition of Arachis Oil. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1922, [iv], **31**, 567--570).—When arachis oil is passed over an alumina-copper catalyst at 600° and the product freed from acids and then hydrogenated over nickel at 180–200° hydrocarbons of the methane and benzene series are obtained. Amongst the aromatic hydrocarbons, benzene, toluene, and m-xylene were identified.

W. G.

Lignoceric Acid and its Derivatives. PERCY BRIGL and EDGAR FUCHS. (*Z. physiol. Chem.*, 1922, **119**, 280—311).—The so-called lignoceric acid, m. p. 78–91°, from beechwood tar is a mixture from which can be separated an acid, m. p. 85°, identical with tetracosic acid, $\text{CH}_3(\text{CH}_2)_{22}\text{CO}_2\text{H}$ (methyl ester, m. p. 60°, phenyl ester, m. p. 70.5°), prepared synthetically from behenic acid (cf. Myer, Brod, and Soyka, A., 1913, i, 1151, and Brigl, A., 1916,

i, 463). The other component of crude lignoceric acid has the same empirical formula and appears to be also a normal tetracosic acid. It melts at 74° , and it is suggested that this may be a case of a peculiar kind of isomerism, due to the possibility of the carbon chain of a fatty acid existing as a right- or left-handed spiral.

Lignocerin, the wax associated with lignoceric acid, after repeated recrystallisation melts at 79° , and has the formula $C_{48}H_{96}O_2$. On hydrolysis with alcoholic potash, it gives (1) an acid identical with crude lignoceric acid, m. p. 79° , from which pure lignoceric acid, m. p. 85° , can be separated, and (2) *lignoceryl alcohol*, $C_{24}H_{50}O$, m. p. 76° (*acetate*, fine, felted needles, m. p. 57°). On fusion with potash, *lignoceryl alcohol* yields the above-mentioned tetracosic acid of m. p. 74° , and thus is not pure *n*-tetracosyl alcohol. To verify this, *n*-tetracosyl alcohol has been prepared by the reduction of the phenyl ester of *n*-tetracosic acid by sodium in alcohol and is found to melt at 77.5° and give an *acetate*, concentric needles, m. p. 57° , and a *benzoate*, m. p. 61.5° . In the preparation of tetracosic acid the methods previously employed are used (Brigl, *loc. cit.*) except that in the reduction of behenic acid to docosyl alcohol by sodium and alcohol the *phenyl ester*, fine needles, m. p. 66° , is used instead of an alkyl ester.

The preparation of the following waxes from the corresponding alcohols and acid chlorides (in chloroform solution in the presence of quinoline) are described; *cetyl palmitate*, m. p. 53° ; *docosyl behenate*, white, lustrous scales, m. p. 75° ; and *n*-tetracosyl *tetracosate*, m. p. 80.5° .

W. O. K.

The Actual State of the Chemistry of the Fats. ÉMILE ANDRÉ (*Bull. Soc. chim.*, 1922, [iv], 31, 459—525).—A useful summary of the present state of knowledge of the chemistry of the fats, including an outline of analytical methods, separation and identification of glycerides, and a discussion of the constitutions of the fats.

W. G.

Erucic Acid and Erucic Anhydride. III. D. HOLDE and C. WILKE (*Z. angew. Chem.*, 1922, 35, 289—291; cf. this vol. i, 317, 519).—A detailed account is given of the methods tried and that finally adopted for the preparation of pure erucic acid from rape oil. The fractional distillation of the esters obtained by the methylation of the oil gave a methyl erucate, b. p. $243-248^{\circ}/33$ mm., $216-225^{\circ}/4$ mm., from which on hydrolysis an erucic acid was obtained which, although having a sharp m. p. 34° , and the correct molecular weight of titration, showed a low iodine value, 71—72, indicating the presence of about 5% of saturated acids. Attempts to separate these by extraction of the lead salts with organic solvents such as ether, light petroleum, or chloroform failed, as the saturated acid salts also dissolved in presence of the large excess of lead erucate, nor could the iodine value of the impure acid be raised by fractional precipitation with lead or magnesium acetate of a preparation which had previously been

partly purified through the methyl ester and recrystallisation from alcohol. The pure acid with an iodine value of 75.02 was eventually obtained by recrystallising the crude acid from alcohol first at temperatures below 0° to remove liquid unsaturated acids, and then at above 0° to remove the greater part of the saturated acids, and finally fractionally precipitating this product with a saturated alcoholic solution of lithium acetate whereby the saturated acids were thrown down first. The pure acid melts at 33.5° . Erucic anhydride was prepared by heating the acid with acetic anhydride in a sealed tube at 170° for seven hours. After purification, it formed microscopic, white prisms, m. p. 46° . It is decomposed by boiling water, boiling alcohol, and cold alcoholic hydroxide solutions, but it is stable towards cold dilute hydrochloric acid and aqueous alkali hydroxides. G. F. M.

Humoceric Acid. OSSIAN ASCHAN (*Finska Kem. samfundets Medd.*, 1921, **30**, 37—38).—A new substance was isolated from peat and designated *humoceric acid*. It has the composition $C_{18}H_{34}O_2$, m. p. $72-73^{\circ}$, separates in colourless crystals from light petroleum and methyl alcohol, does not give the cholesterol colour reactions, and reacts instantly with Baeyer's reagent. It is not identical with lignoceric acid, $C_{24}H_{48}O_2$, m. p. 80° .

CHEMICAL ABSTRACTS.

Synthesis of α -Hydroxyisopentacosic Acid and its Bearing on the Structure of Cerebronic Acid. P. A. LEVENE and F. A. TAYLOR (*J. Biol. Chem.*, 1922, **52**, 227—240).—It has been shown that cerebronic acid is an α -hydroxypentacosic acid (Levene and Jacobs, A., 1912, i, 936) and is converted on oxidation into a tetracosic acid (Levene and West, A., 1913, i, 587) which is identical with lignoceric acid. According to Meyer, Brod, and Soyka (A., 1913, i, 1151), and to Levene and West (A., 1914, i, 1123), lignoceric acid differs from *n*-tetracosic acid, a result which indicates that cerebronic acid is not a normal fatty acid. Brigl (A., 1916, i, 463), however, from a comparison with the synthetic acid, considers that cerebronic acid is normal α -hydroxypentacosic acid. The present authors attribute this result to imperfect racemisation, with consequent incorrect melting point, of the natural acid, and advance the following further proof of the identity of tetracosic acid (from cerebronic acid) and lignoceric acid (cf. Brigl, this vol., i, 712). Tetracosic acid, obtained from cerebronic acid, and lignoceric acid, from peanut oil, were converted by the same series of reactions into α -hydroxypentacosic acid. Two series of compounds were thus obtained of which the corresponding members were found to be identical, thus establishing the identity of the first two acids and showing, therefore, that cerebronic acid does not contain a normal chain and is, consequently, α -hydroxy-lignoceropentacosic acid.

Lignoceric acid and tetracosic acid (from cerebronic acid) were converted into lignoceryl iodide. The latter, when boiled in

alcoholic solution with potassium cyanide, gave *lignoceryl cyanide*, $C_{24}H_{49}ON$, m. p. 56.5° , which on hydrolysis with alcoholic sodium hydroxide yielded *isopentacosic acid*, $C_{24}H_{49}\cdot CO_2H$, m. p. 78.5° . By bromination, α -*bromoisopentacosic acid*, $C_{24}H_{47}Br\cdot CO_2H$, m. p. 70° , was obtained, from which *dl-cerebronic acid*, $OH\cdot C_{24}H_{48}\cdot CO_2H$, m. p. 92.5° , was produced by boiling with aqueous sodium hydroxide. *Ethyl isopentacosate*, $C_{24}H_{49}\cdot CO_2Et$, m. p. 57° , was reduced by sodium and alcohol to *isopentacosyl alcohol*, $C_{24}H_{49}\cdot CH_2\cdot OH$, m. p. 75° , and the alcohol converted into *isopentacosyl iodide*, $C_{24}H_{49}\cdot CH_2I$, m. p. 51.5° , by means of iodine and red phosphorus. The latter, on reduction with zinc and hydrochloric acid, gave *isopentacosane*, $C_{25}H_{52}$, m. p. 56° .

Lignoceric acid was also converted into *isopentacosic acid* by the following reactions: α -hydroxylignoceric acid (cf. Meyer, Brod, and Soyka, *loc. cit.*) was first prepared. This was then oxidised by potassium permanganate in acetone solution to *isotricosic acid*, $C_{22}H_{45}\cdot CO_2H$, m. p. 73.5° . Reduction of *ethyl isotricosate*, $C_{22}H_{43}\cdot CO_2Et$, m. p. 55.5° , with sodium and alcohol gave *isotricosyl alcohol*, $C_{22}H_{45}\cdot CH_2\cdot OH$, m. p. 69° , which when heated with iodine and red phosphorus yielded *isotricosyl iodide*, $C_{22}H_{45}\cdot CH_2I$, m. p. 48° . By condensation with diethyl malonate this was converted into *diethyl isotricosylmalonate*, $C_{22}H_{43}\cdot CH_2\cdot CH(CO_2Et)_2$, m. p. 52.5° , which was then hydrolysed with alcoholic sodium hydroxide to *isotricosylmalonic acid*, $C_{22}H_{45}\cdot CH_2\cdot CH(CO_2H)_2$, m. p. 111° . The latter lost carbon dioxide at 180° , yielding *isopentacosic acid* identical with that obtained above. E. S.

Action of Thionyl Chloride on α -Hydroxy-acids. E. E.

BLAISE and (Mlle) MONTAGNE (*Compt. rend.*, 1922, **174**, 1553—1555; cf. this vol., i. 520).—Thionyl chloride reacts with lactic acid and with α -hydroxyisobutyric acid to give, not the chlorosulphite of the acid chloride, but a new type of compound, which the authors call anhydrosulphites of hydroxy-acids, the compound obtained

from α -hydroxyisobutyric acid having the constitution

$$\begin{array}{c} \text{CO} \cdot \text{O} \\ | \\ \text{CMe}_2 \cdot \text{O} \end{array} \text{SO}.$$

The compound from lactic acid has b. p. $72-74^\circ/19$ mm., and the compound from hydroxyisobutyric acid has b. p. $63^\circ/21$ mm. Both these compounds are decomposed at $120-125^\circ$ at atmospheric pressure, giving off sulphur dioxide and yielding polyactides which with alkalis give the corresponding hydroxy-acids. In contact with moist air, the anhydrosulphites revert to the original acid, and in the case of that from lactic acid an intermediate compound m. p. 90° , having the constitution $SO_2H\cdot O\cdot CHMe\cdot CO_2H$ or $HO\cdot CHMe\cdot CO\cdot O\cdot SO_2H$ was isolated. With alcohols the anhydrosulphites react readily, giving the esters of the hydroxy-acids, and with arylamines they yield the amides of these acids. With phenylhydrazine, on the other hand, they give thionylphenylhydrazine and the hydroxy-acid.

In the original action of the thionyl chloride on lactic acid there is obtained, in addition to the anhydrosulphite, some *α-chloro-propionyloxypropionyl chloride*, $\text{CHMeCl}\cdot\text{CO}_2\cdot\text{CHMe}\cdot\text{COCl}$, b. p. $100-103^\circ/19$ mm., giving an *anilide*, m. p. 116.5° . Similarly, *α-hydroxyisobutyric acid* yields *α-chloroisobutyryloxyisobutyryl chloride*, $\text{CMe}_2\text{Cl}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{COCl}$, b.p. $99-101^\circ/17$ mm., giving an *anilide*, m. p. 115° , and at the same time there is obtained some *α-chloroisobutyryl chloride*, b. p. $113-114^\circ$, and its *anilide*, m. p. $69-70^\circ$. W. G.

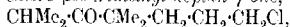
Succinic Acid. UMETARÔ SUZUKI and YOSHIHIKO MATSUYAMA (Japan Pat. 39210).—Ten grams of glutamic acid are gradually heated with 50 grams of concentrated nitric acid and 0.005 gram of vanadium oxide. When the evolution of gas has ceased, the solution is concentrated by evaporation. Succinic acid crystallises out as colourless prisms or plates, the yield being 5–6 grams. Sodium glutamate or gluten and metallic vanadium or vanadates can also be used for the purpose. K. K.

Crystallographic - optical Properties of Calcium Fumarate and Maleate. EDGAR T. WHERRY and RAYMOND M. HANN (*J. Washington Acad. Sci.*, 1922, **12**, 288–296).—Calcium fumarate, $\text{C}_4\text{H}_2\text{O}_4\text{Ca}\cdot 2\text{H}_2\text{O}$, crystallises from water in blade-like crystals belonging to the orthorhombic system, $a:b:c = 0.3970:1:0.3772$; $d\ 1.71 \pm 0.01$. They are optically negative with extreme double refraction; the mean refractive index is 1.539. Calcium maleate, $\text{C}_4\text{H}_2\text{O}_4\text{Ca}\cdot\text{H}_2\text{O}$, forms groups of interlacing needles, orthorhombic prisms the end faces of which are not well developed; $a:b:c = 0.779:1:0.643$; $d\ 1.84 \pm 0.01$. The double refraction is negative and weaker than in the case of the fumarate; the mean value of n is 1.571. There is no simple space relation between the two salts. The molecular refractions R , calculated from the formula $R = V(n^2 - 1)/(n^2 + 1)$, where V is the molecular volume, are, for the fumarate 34.8, maleate, 30.8, the corresponding values calculated from the atomic constituents being 31.7 and 27.8. The refractivities due to structure are therefore 3.3 and 3.0, respectively, the higher value in the case of the fumarate being due to the fact that the ring system formed by the calcium atom bridging the two acid groups in the molecule is more complex in the fumarate than in the maleate. E. H. R.

Conditions Underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. IV. Products Formed from Halogen Derivatives of Muconic Acid. The Constitution of Muconic Acid. JEAN PEDIGE CHARLES CHANDRASENA and CHRISTOPHER KELK INGOLD (*T.*, 1922, **121**, 1306–1319).

Synthesis of the Polyacetic Acids of Methane. VI. Methanetriacetic Acid and its Unstable Esters. CHRISTOPHER KELK INGOLD and EDWARD ARTHUR PERREN (*T.*, 1922, **121**, 1414–1420).

The Action of Trimethylene Chlorobromide on some Aliphatic Ketones. (MILLE) HÉLÈNE BILLON (*Compt. rend.*, 1922, **174**, 1708—1711).—Haller and Bauer have shown that the sodium derivatives of dialkylacetophenones react with trimethylene chlorobromide to give δ -chloro-ketones (cf. A., 1911, i, 651). This is now shown to be true of aliphatic ketones. The resulting chloro-compounds react with dimethyl- or diethyl-amine to give dimethyl-amino- and diethylamino-compounds respectively. The compounds described are η -chloro- $\beta\delta\delta$ -trimethyl-heptan- γ -one,



d.p. 120°—122°/20 mm.; ϵ -dimethylamino- $\beta\delta\delta$ -trimethylheptan- α -one, b. p. 120°/22 mm.; ϵ -diethylamino- $\beta\delta\delta$ -trimethylheptan- α -one, b. p. 126°—128°/20 mm.; η -chloro- $\beta\beta\delta\delta$ -tetramethylheptan- γ -one, b. p. 110°—112°/12 mm.; ϵ -dimethylamino- $\beta\beta\delta\delta$ -tetramethylheptan- α -one, b. p. 126°—138°/20 mm.; η -chloro- $\gamma\gamma\epsilon\epsilon$ -tetramethyl-octan- δ -one, b. p. 124°/16 mm.; η -dimethylamino- $\gamma\gamma\epsilon\epsilon$ -tetramethyloctan- δ -one, b. p. 138°—140°/20 mm. Under similar conditions, pinacolin does not give a chloro-compound but a ketone which is apparently

pinacolyleyclobutane, $\text{CH}_2\begin{matrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{matrix} \text{CH-CO-CMe}_2$, b. p. 97°/17 mm.
W. G.

The Chlorohydrin of Mesityl Oxide and its Transformation into the Chlorohydrin of Tetramethylglycerol. PASTUREAU and HENRI BERNARD (*Compt. rend.*, 1922, **174**, 1555—1557).—Mesityl oxide reacts with a mixture of calcium hypochlorite and boric acid to give its chlorohydrin [α -chloro- β -hydroxyisobutyl methyl ketone], $\text{HO-CMe}_2\text{-CHCl-COMe}$, b. p. 81°/10 mm., and this with magnesium methyl iodide gives a compound which on decomposition with water yields tetramethylglycerol chlorohydrin (γ -chloro- $\beta\delta$ -dihydroxy- $\beta\delta$ -dimethylpentane), $\text{HO-CMe}_2\text{-CHCl-CMe}_2\text{-OH}$, m. p. 60°.
W. G.

2:3:6-Trimethyl Glucose. JAMES COLQUHOUN IRVINE and EDMUND LANGLEY HIRST (*T.*, 1922, **121**, 1213—1223).

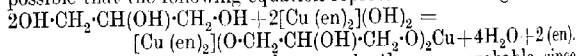
The Constitution and Rotatory Powers of Mannitol and Fructose Complexes Formed in Solutions Containing Boric Acid and Sodium Hydroxide. GEORGE VAN BARNEVELD GILMOUR (*T.*, 1922, **121**, 1333—1340).

The Action of Ozone on Pure Solutions of Lactose. C. W. SCHONEBAUM (*Rec. trav. chim.*, 1922, **41**, 422—424; cf. *Annalen*, 1859, **110**, 86).—It has been stated that lactose is not decomposed by ozone. The author finds that this is only true of neutral and acid solutions at both ordinary temperatures and 70°. In alkaline solution of 0.1N concentration, 30% of the lactose is decomposed after three hours' ozonisation, whilst at 70° rapid neutralisation of the alkali takes place. This is due to the formation of formic
c c*

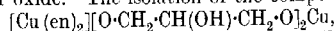
acid, the primary decomposition product. In 4*N*-alkali, carbon dioxide is formed after one hour; this and water are the final products of ozonisation. Ozone of low concentration was used. H. J. E.

The Colloidal Nature of Saccharated Iron. C. MANNICH and C. A. ROJAHN (*Ber. deut. Pharm. Ges.*, 1922, **32**, 158—166).—“Saccharated” iron contains the metal as colloidal ferric hydroxide, and is in no sense a compound of sugar and iron. It gives a colloidal solution in water in consequence of the sugar and the alkali which also must be present. That none of the sugar is chemically combined with the metal appears certain from the fact that the colloid isolated by dialysis, by ultra-filtration, or by kataphoresis contains an amount of sugar varying according to the method adopted from 16.6 to 25.5%. An average value would require 16 atoms of iron to 1 mol. of sugar, which is a remotely improbable combination. It is concluded, therefore, that the iron is present entirely as colloidal hydroxide, which absorbs a certain amount of both sugar and alkali. The solution differs from dialysed solution of iron (*Liquor Ferri Dialysatus*) in that the particles are negatively charged in the former and positively in the latter, and the addition of 4–8 drops of this to 5 c.c. of 5% solutions of saccharated iron results in complete flocculation. A similar precipitation of the iron is caused by neutralising the alkali with, for example, acetic acid or carbon dioxide; like many other colloids it is absorbed by relatively small quantities of charcoal, and a colourless filtrate may be obtained in which iron is undetectable. G. F. M.

Alkaline Copper Oxide Solutions and Copper Oxide-Ammine-Cellulose Solutions. II. WILHELM TRAUBE (*Ber.*, 1922, **55**, [B], 1899—1912).—In a previous communication (this vol., i, 115), the action between copper ethylenediamine hydroxide and glycerol has been considered to take place in accordance with the equations: $2\text{C}_2\text{H}_5\text{O}_2\cdot\text{CH}_2\cdot\text{OH} + [\text{Cu}(\text{en})_2](\text{OH})_2 \rightleftharpoons 2\text{H}_2\text{O} + [\text{Cu}(\text{en})_2](\text{O}\cdot\text{CH}_2\cdot\text{C}_2\text{H}_5\text{O}_2)_2$ and $[\text{Cu}(\text{en})_2](\text{O}\cdot\text{CH}_2\cdot\text{C}_2\text{H}_5\text{O}_2)_2 + \text{Cu}(\text{OH})_2 = [\text{Cu}(\text{en})_2][\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{O}]_2\text{Cu} + 2\text{H}_2\text{O}$. It is also possible that the following equation represents the change:



The second possibility is now shown to be the more probable, since the reaction occurs with liberation of considerable amounts of ethylenediamine as is proved by the ability of the solution to dissolve silver oxide. The isolation of the compound



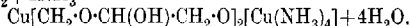
in an almost homogeneous condition is now described.

The conclusions thus drawn in the studies with glycerol can be extended to other polyhydroxy-substances, notably cellulose. The ability of copper oxide-ethylenediamine-cellulose solutions to dissolve further quantities of copper oxide depends on the liberation of ethylenediamine, and the behaviour of Schweizer's solution may

be explained similarly. The difference* between the behaviour of the copper bases towards polyhydroxy-compounds and those of the metals silver, cobalt, nickel, zinc, and cadmium is accounted for, since only the former is able to form complexes in which the metallic atom is fixed directly to the hydroxy-group of the polyhydroxy-compound. An uncertainty, however, appears to exist in the case of cobalt, since, according to the literature, the precipitation of this metal from its solutions as hydroxide by means of alkali is hindered by the presence of glycerol in the same manner as is the precipitation of copper hydroxide from copper solutions; the exception is only apparent, however, since the cobalt hydroxide is present in the colloidal state (and not as the glycerate) and can be precipitated completely by barium sulphate.

Confirmation of the results obtained with copper ammine hydroxides and polyhydroxy-compounds is afforded by the behaviour of the former towards biuret. Copper ethylenediamine hydroxide and biuret give the compound $C_8H_{22}O_4N_{10}Cu_2H_2O$, lustrous needles, m. p. 198° (decomp.), which is formed in accordance with the scheme: $2C_2H_5O_2N_3 + 2[Cu(en)_2](OH)_2 = [Cu(en)_2](C_2H_3O_2N_3)_2Cu + 4H_2O + 2(en)$.

It has been assumed that the solution of copper hydroxide in ammoniacal glycerol occurs in accordance with the equation: $2C_3H_5O_3 + 2Cu(OH)_2 + 4NH_3 =$



The corresponding derivative from biuret,
 $[Cu(NH_3)_4][C_2H_3O_2N_3)_2Cu]$

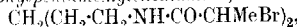
has been analysed.

H. W.

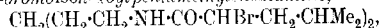
Oxycellulose. EMIL HEUSER AND FRITZ STÖCKIGT (*Cellulosechemie*, 1922, **3**, 61—74).—The formation of furfuraldehyde-yielding groups is one of the constitutional characteristics of oxycellulose. The quantity of furfuraldehyde obtained is not large. Whilst well-purified cotton yielded 0.3%, oxycellulose preparations generally yielded less than 1.0%. Higher yields of furfuraldehyde were recorded when the oxidation was carried out by chromic acid in such quantities that substantial losses of cellulose were incurred. For instance, an oxycellulose prepared by chromic acid with a yield of 66% gave 2.14% of furfuraldehyde, and, in an extreme case, 12.5% of oxycellulose was obtained having a furfuraldehyde value of 3.89%. The presence of carboxylic groups in oxycellulose has often been suggested, but definite proof is now afforded by the observation that on distillation with 12% hydrochloric acid, oxycellulose yields small quantities of carbon dioxide. The carboxyl value of oxycellulose has been estimated by Lefèvre's method for the estimation of glycuronic acid; the values obtained were generally less than 1.0%, but in the case of highly oxidised chromic acid oxycellulose values up to 1.32% were obtained. On hydrolysis with 1% sulphuric acid under pressure, oxycellulose gave a residue of hydrocellulose with low furfuralde-

hyde and carboxyl values; and a solution containing the characteristic oxidised component. This substance yielded a barium salt having many of the characteristic properties of barium glycerurate, but differing from that salt in its barium content. On complete hydrolysis by Willstätter's method, oxycellulose yielded a solution having a dextrose value about 10% lower than that obtained from cellulose and hydrocellulose; the residue from the digestion of oxycellulose with dilute sulphuric acid gave the normal dextrose value of hydrocellulose. Hence it is concluded that oxycellulose, prepared as a residue from the action of oxidising agents on cellulose, consists for the major part of cellulose in which there exists, either as a mixture or in combination, a small quantity of an intermediate complex, formed of a combination of cellulose with an oxidation product. This oxidation product has the characters of an aldehyde-carboxylic acid, and is probably derived either from a terminal alcoholic group of a cellobiose residue or from an aldehyde group developed by hydrolysis. J. F. B.

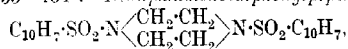
New Diamine Compounds. PETER BERGELL (*Z. physiol. Chem.*, 1922, **120**, 220—226).—The following compounds were prepared by the interaction of the respective bases and acid chlorides: *Di-α-bromopropionylpentamethylenediamine*,



crystallises in radiating needles arranged spherically, m. p. 135—136°. *Di-α-bromoisobutyrylpentamethylenediamine*,



crystallises in leaflets, m. p. 127—128°. *Di-β-naphthalenesulphonylpentamethylenediamine*, $\text{CH}_2(\text{CH}_2\text{CH}_2\text{NH}\cdot\text{SO}_2\cdot\text{C}_{10}\text{H}_7)_2$, crystallises in lustrous leaflets, m. p. 147—149°. *β-Naphthalenesulphonylpiperidine*, $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{N}\langle\text{CH}_2\text{CH}_2\rangle\text{CH}_2$, is a silky white precipitate, m. p. 133—134°. *Dinaphthalenesulphonylpiperazine*,



is an indistinctly microcrystalline precipitate.

S. S. Z.

Betaines. I. Theory of Betaines. PAUL P. PFEIFFER (*Ber.*, 1922, **55**, [B], 1762—1769).—It is customary to ascribe a cyclic structure to the betaines, which, however, do not obey the usual stereochemical laws of ring closure. This is particularly noticeable with the betaines of the aromatic series in which compounds derived from *p*- and *m*- as well as those derived from *o*-aminobenzoic acid are known. Since, however, the entire chemical behaviour of the betaines causes them to be regarded as intramolecular quaternary ammonium salts, it is reasonable to apply to them the recent ideas on the constitution of salts as deduced by Debye and Scherrer, and to consider that positive and negative ionic charges are located in the molecule which may be formulated,

$-OOC-R-NMe_3^+$. The sole difference in the structure of sodium chloride and betaine is that the ions are separated in the former and united by a chain of atoms in the latter. The formation of a betaine has, in principle, no connexion with ring closure; the electric polar charges attract one another, but the extent to which they actually approach one another depends on the configuration of the molecule. With para-betaines the *trans*-configuration of the molecule inhibits the approach of the groups, COO^- and NMe_3^+ , and ring closure does not occur. This is true also of the meta-compounds. With the ortho-products, on the other hand, ring closure is possible. The views thus put forward for the betaines are applicable to the amino-acids.

The crystals of amino-acids or betaines are not exactly similar to those of salts or organic compounds. It must be assumed that in them, as in ordinary organic substances, the molecular lattice structure is pronounced, but between the single molecules, in accordance with their bipolar nature, strong electrostatic forces are operative such as only occur otherwise in ionic lattices. It may therefore be stated that the amino-acids and betaines form molecular lattices with the general character of ionic lattices. An explanation is thereby afforded of the extremely high melting or decomposition points of these substances which are otherwise not related to their molecular complexity. The sparing solubility in organic media likewise receives an explanation.

Similar stereochemical difficulties arise in the elucidation of the constitution of salts of dibasic organic acids with bivalent metals.

The co-ordination formulae, for example, $\left[\begin{smallmatrix} O \\ \diagup \\ C - R - C \\ \diagdown \\ O \end{smallmatrix} \right]^{2-} Ca^{++}$,

are probably to be assigned to them, a normal ring not being present.

H. W.

Transformation of Alkylated Malonic Acids into α -Amino-acids. II. Syntheses of β -Phenyl- α -alanine and of α -Amino-*n*-butyric Acid. THEODOR CURTIUS and WILHELM SIEBER (*Ber.*, 1922, 55, [B], 1543—1558; cf. Curtius and Sieber, A., 1921, i, 653).—It has been shown previously that potassium hydrazidomalonate is convertible into glycine in accordance with the scheme: $CO_2K \cdot CH_2 \cdot CO \cdot NH \cdot NH_2 \rightarrow CO_2H \cdot CH_2 \cdot CO \cdot N_3 \xrightarrow{-N_2} [CO_2H \cdot CH_2 \cdot N \cdot CO] \xrightarrow{+H^+} NH_2 \cdot CH_2 \cdot CO_2H + CO_2$. Since also it was found that the yield of α -alanine from methylmalonazidic acid is better than that of glycine from the lower homologue, the possibility of the peculiar applicability of the process to the more highly substituted acids has been examined. In this respect, the results are somewhat disappointing, since ethylmalonazidic acid is extensively hydrolysed by boiling water to hydrazoic acid and ethylmalonic acid whereas benzylmalonazidic acid is insoluble in water and remains unaffected. In boiling ethereal solution, ethyl- and benzylmalonazidic acids are converted into the corresponding carboxylic

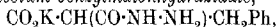
anhydrides, $\text{CH}_2\text{R}\cdot\text{CH}\begin{matrix} \text{CO}\cdot\text{O} \\ | \\ \text{NH}\cdot\text{CO} \end{matrix}$ ($\text{R}=\text{Ph}$ or Me), diketopiperazines,

$\text{CHR}\begin{matrix} \text{CO}\cdot\text{NH} \\ | \\ \text{NH}\cdot\text{CO} \end{matrix}\text{CHR}$, and complex anhydrides, $\left(\text{R}\cdot\text{CH}\begin{matrix} \text{CO} \\ | \\ \text{NH} \end{matrix}\right)_x$,

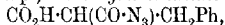
all of which are hydrolysed by concentrated hydrochloric acid under pressure with quantitative production of the hydrochlorides of the simple amino-acids.

When solutions of the azidic acids in indifferent media are boiled, explosions occasionally take place without any apparent cause, as, for example, in dilute ethereal solutions from which solid has not separated. The conversion of the acids into the corresponding urethanes is therefore effected by the addition of absolute ethyl alcohol to the dry ethereal solution and subsequent slow distillation of the ether. The urethanes are thus obtained as oily liquids which generally contain small amounts of the corresponding polymolecular anhydride, and, less frequently, of the diketopiperazine derivative. The crude product is directly converted into the amino-acid hydrochloride by treatment with hydrochloric acid in sealed tubes. The success of these methods of synthesising amino-acids depends greatly on the purity of the initial materials and the reagents.

The conditions have been established under which ethyl benzylmalonate is transformed almost quantitatively by alcoholic potassium hydroxide solution into potassium ethyl benzylmalonate. The latter is converted by anhydrous hydrazine in absolute alcoholic solution into *potassium benzylmalonhydrazidate*,



anisotropic platelets; the corresponding *acid* crystallises in small prisms, m. p. 163° , and gives the *benzylidene* derivative, $\text{CO}_2\text{H}\cdot\text{CH}(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh})\cdot\text{CH}_2\text{Ph}$, rectangular, anisotropic platelets, m. p. 152° (decomp.). *Benzylmalonazidic acid*,



is a heavy, yellow liquid which could not be caused to solidify. It is converted in boiling ethereal solution into phenylalanine-*N*-carboxylic anhydride, m. p. $127-128^\circ$ (decomp.) [the constitution of which is established by the observation that it is converted by cold aniline into carbon dioxide and *phenylalanineanilide*, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NHPh}$, small, thin, feebly anisotropic prisms, m. p. $160-161^\circ$], polymolecular phenylalanine anhydride and 2:5-diketo-3:6-dibenzylpiperazine. *Phenylalanine hydrochloride* crystallises in anisotropic prisms, m. p. $234-235^\circ$. *Benzylmalonazidic acid* decomposes in boiling chloroform with the production of somewhat ill-defined products which are convertible into phenylalanine hydrochloride.

Ethylcarbonatophenylalanine and *methylcarbonatophenylalanine* could only be obtained as liquids which could not be caused to solidify or distilled without decomposition.

Potassium ethyl ethylmalonate is transformed into *potassium*

ethyl malonhydrazidate, a very hygroscopic, crystalline mass; the *benzylidene* compound of the corresponding free acid, $\text{CHEt}(\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CHPh})\cdot\text{CO}_2\text{H}$, prisms, m. p. 144° (decomp.), is described. Diazotisation of the hydrazidic acid leads to the formation of a substance, colourless, slender needles, m. p. $82-83^\circ$, which has not been investigated completely and *ethylmalonazidic acid*, a pale yellow liquid. Decomposition of the latter in boiling ethereal solution leads to the production of ethylmalonic acid and the

carboxylic anhydride, $\text{CHEt}\begin{matrix} \text{CO}\cdot\text{O} \\ | \\ \text{NH}\cdot\text{CO} \end{matrix}$, m. p. 113° (decomp.), which is converted by warm alcohol into polymolecular α -amino-*n*-butyric

anhydride, $\left[\text{CHEt}\begin{matrix} \text{CO} \\ | \\ \text{NH} \end{matrix}\right]_x$, m. p. above 300° after becoming brown at about 250° . α -Aminobutyric acid hydrochloride crystallises in coarse, anisotropic prisms, m. p. 182° .

*Methylcarbonato- α -amino-*n*-butyric acid*, $\text{CO}_2\text{Me}\cdot\text{NH}\cdot\text{CHEt}\cdot\text{CO}_2\text{H}$, is obtained as a liquid which cannot be caused to solidify or distilled without decomposition by the action of a mixture of methyl alcohol and ether on ethylmalonazidic acid; it is transformed by concentrated hydrochloric acid into α -aminobutyric acid hydrochloride.

Ethyl α -amino-*n*-butyrate hydrochloride has m. p. 142° . H. W.

The Synthetic Preparation of Carbamide from Ammonia.

C. MATIGNON and M. FRÉJACQUES (*Ann. Chim.*, 1922, [ix], **17**, 257—304).—A more detailed account of work already published (*A.*, 1920, ii, 250; 1921, ii, 33; this vol., ii, 272, 445). W. G.

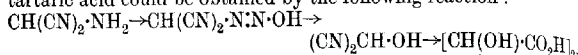
Semicarbazide Hydrochloride. HIDEO OCHI (Japan Pat., 39219).—Semicarbazide hydrochloride is prepared from nitro-carbamide by electrolytic reduction. As catholyte a mixture of nitro-carbamide and ten times the quantity of 10% hydrochloric acid is used and as anodal solution, 25% sulphuric acid. As a cathode, a lead cylinder is used and a spiral of lead tube as an anode, separated by means of a porous cell. The reaction is conducted at $0-5^\circ$, using a current of 1 ampere per sq. dm. and 4 volts. The product is obtained by evaporation of the catholyte in a vacuum. K. K.

Products of Polymerisation of Hydrocyanic Acid.

E. GRISZKIEWICZ-TROCHIMOWSKI (*Roczniki Chemji*, 1921, **1**, 468—478).—The constitution $\text{NH}_2\cdot\text{CH}(\text{CN})_2$ has been suggested for the trimeride of hydrocyanic acid. In order to verify the presence of the amino-group, two reactions were investigated, namely, condensation with aldehydes and the action of nitrous acid. The first reaction followed the course expected, and the following compounds were obtained. With salicylaldehyde, the *salicylidene* derivative, $\text{CH}(\text{CN})_2\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, yellowish-green needles, m. p. about 235° (decomp.). With anisaldehyde, the *anisylidene* derivative, $\text{CH}(\text{CN})_2\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$. With benzalde-

hyde, the *benzylidene* derivative, $\text{CH}(\text{CN})_2\cdot\text{N}\cdot\text{CHPh}$, brown plates, m. p. 190° (decomp.). A *benzoyl* derivative of the trimeride was also prepared, brown plates, m. p. 220° (decomp.), together with its unstable *hydrochloride*.

The results with nitrous acid were not those expected; it was thought that a diazo-compound would be formed, from which tartaric acid could be obtained by the following reaction:—



The product of the reaction does not, however, decompose on boiling; it is obtained from the solution in orange prisms, m. p. about 145° , and is shown to be 4 : 5-dicyano-1 : 2 : 3-triazole. On sublimation at 140° , this is obtained in a colourless modification.

for which the constitution $\text{NH} \begin{array}{c} \text{N}\cdot\text{C}\cdot\text{CN} \\ \text{N}\cdot\text{C}\cdot\text{CN} \end{array}$ is suggested.

The silver, copper, barium, potassium, and ammonium salts of the dicyanotriazole were prepared, also its 1-methyl derivative, m. p. $57\cdot5$ — $58\cdot5^\circ$.

On hydrolysis with hydrochloric acid, the 4-amide of 1 : 2 : 3-triazole-4 : 5-dicarboxylic acid is produced, m. p. 275° . By passing hydrogen chloride through an ethereal solution of the substance, the ethyl ester of 4-cyano-1 : 2 : 3-triazole-5-carboxylic acid is obtained, m. p. 114 — 115° , whence the acid, m. p. 225 — 226° , is obtained, and from this by hydrolysis with sulphuric acid the 4 : 5-dicarboxylic acid, m. p. 195 — 196° , is produced.

It is suggested that the dicyanotriazole may be produced from the nitrous acid by condensation of a diazotised molecule of it with an undiazotised one. The results both with aldehydes and with nitrous acid, therefore, support the view that the trimeride of hydrocyanic acid is $\text{CH}(\text{CN})_2\cdot\text{NH}_2$. R. T.

Equilibrium in the System Ammonia-Mercuric Cyanide.

S. R. BRINKLEY (*J. Amer. Chem. Soc.*, 1922, **44**, 1210—1216).—The vapour pressures of ammonia in the binary system ammonia-mercuric cyanide have been determined at 0° over a range from 370 mm. to 1600 mm., and in the ternary system, ammonia-water-mercury cyanide the solubility curve has been determined at the same temperature. It is shown that the vapour pressures of the solutions are far below those required by Raoult's law. The solid products, $\text{Hg}(\text{CN})_2\cdot\text{NH}_3$ and $\text{Hg}(\text{CN})_2\cdot 2\text{NH}_3$, have been isolated and have been shown to be the only additive compounds between these two components at 0° . J. F. S.

The Solubility of Potassium Ferrocyanide. REECE H. VALLANCE (*Chem. News*, 1922, **125**, 7).—The solubility of potassium ferrocyanide at temperatures up to 30° has been determined with the following results expressed in grams per 100 grams of saturated solution: $10\cdot4^\circ$, 17·541; $13\cdot8^\circ$, 19·067; $16\cdot9^\circ$, 20·862; $20\cdot4^\circ$, 21·953; $23\cdot1^\circ$, 23·074; $25\cdot0^\circ$, 23·971. Determinations by previous

workers have given widely varying results. Evidence was obtained of a transition point in the neighbourhood of 18° . G. F. M.

Thermochemical Researches on Oximes. II. The Stereoisomeric Ethyl Esters of Oximinoacetoacetic Acid.

ALICJA DORABIALSKA (*Roczniki Chemji*, 1921, **1**, 448—467).—Ethyl oximinoacetoacetate has been described by Jovitschitsch (A., 1896, i, 82), who states that it may exist in two forms, both oils. The β -form, according to him, differs from the α -, in that its sodium hydroxide solution on acidification evolves carbon dioxide. The conversion is stated by him to be effected by the action of nitrous and sulphuric acids on the ester. Bouveault and Wahl (A., 1905, i, 506), however, only obtained one form, m. p. 56° , and the author finds that no conversion is effected by their method. The α -isomeride is prepared in various ways, including a hitherto undescribed method, whereby it is obtained from nitrosyl chloride and acetoacetic acid ester. The purest form has m. p. 56.7° . A monohydrate, m. p. 45° , is obtained in rhombic plates, and from analyses of the compound m. p. 56.7° it is concluded that it contains at least 28.7% of the hydrate, which can be isomorphous with it, and has the same space structure. It is found that if the α -isomeride be left in strongly acid solution, and this is extracted with ether, a new modification is obtained, m. p. 49° . This is the β -ester, mixed with, at the very least, 19% of the α -form. On solution in alkalis and reprecipitation, the α -form is regenerated. Attempts to produce a hydrochloride failed. Both forms were examined thermochemically. The reactions studied were the formation of the sodium salt of both forms, from solutions and from the solid esters. Further, the heat of reaction with hydrochloric acid in ether solution, q_{HCl} , was measured, and that of the solution of the oximes in water (S). The following values were obtained for the α -ester: q 8.85, q_{HCl} 2.86, Q 4.83, and S -3.77, and for the mixed $\alpha\beta$ -ester: q_{HCl} 4.96, Q 6.14, and S -3.70. The heat of formation of the sodium salt is, for solutions of the esters, given by q , and with solid esters by Q , all figures being given in calories per millimole.

For the β -ester, q is calculated to be 6.72, whilst for the monohydrate it is 8.77. The degree of hydrolysis of the sodium salt is found to be zero. The heat of reaction of the ester with a solution of nitrosyl chloride in toluene is 31.77 cal. per millimole.

R. T.

The Variation of Refractive Index and Density of Benzene with Temperature. WILLIAM BAYLEY PARKER and GARTHA THOMPSON (T., 1922, **121**, 1341—1343).

Equilibrium in Liquid Mixtures of Ammonia and Xylene. CHARLES A. KRAUS and EDWARD H. ZEITFUCHS (*J. Amer. Chem. Soc.*, 1922, **44**, 1249—1260).—The total vapour pressure of liquid mixtures of ammonia and *m*-xylene has been determined for the entire range of compositions at 8° , 10° , 12° , 14° , 15° , 17° , and 20° . Mixtures of liquid ammonia and *m*-xylene

exhibit a critical end-point at 14.7° at a pressure of 6.85 atm. and a composition of 81.4 mol. % of ammonia. The composition of the liquid phases in equilibrium with each other in the three-phase system has been determined at all the temperatures mentioned above and at -33.5° . At lower temperatures, the percentage of ammonia in the phase rich in xylene decreases very rapidly with the temperature.

J. F. S.

The Chlorination of Benzyl Chloride. S. C. J. OLIVIER (*Rec. trav. chim.*, 1922, **41**, 419—421; cf. Beilstein and Kuhlberg, *Annalen*, 1868, **146**, 320).—The preparation of *p*-chlorobenzyl chloride by chlorination of benzyl chloride in presence of iodine is unsatisfactory, as, in addition to iodine derivatives which are difficult to separate, considerable quantities of the ortho- and traces of the meta-isomeric are also obtained. The product is not identical, as stated, with that obtained by chlorination of boiling *p*-chlorotoluene.

H. J. E.

Nitrotoluenes. VIII. Binary Systems of *m*-Nitrotoluene with another Nitrotoluene. JAMES M. BELL and JOSEPH L. MCEWEN. (*J. Ind. Eng. Chem.*, 1922, **14**, 536—537; cf. A., 1921, i, 234, 330).—Freezing-point curves have been constructed for binary mixtures of *m*-nitrotoluene with *o*- and *p*-nitrotoluene, respectively. In the system *m*-nitrotoluene-*p*-nitrotoluene a single eutectic exists at -2.8° corresponding with 37% of the para-constituent, whilst in the system *m*-nitrotoluene-*o*-nitrotoluene the eutectic lies at -31.65° and corresponds with 48% of the meta-constituent. In the latter case, a metastable curve is indicated which would have a eutectic at about -39° , corresponding with about 46% of the meta-constituent.

J. F. S.

Organic Radicles with Quadrivalent Nitrogen. III. HEINRICH WIELAND and FRITZ KÖGL (*Ber.*, 1922, **55**, [B], 1798—1803).—An extension of the work of Wieland and Roth (A., 1920, i, 304).

Di-*p*-tolylnitric oxide has been shown to yield a pale yellow, unstable, crystalline, additive compound with nitric oxide; this is now identified as di-*p*-tolylnitroamine, $(C_6H_4Me)_2N \cdot NO$, since it is converted by hydrogen in the presence of palladium black into ammonia and di-*p*-tolylamine.

Diphenyl-nitrogen oxide reacts with tetra-*p*-anisylhydrazine in absolute ethereal solution, with the formation of di-*p*-anisylnitrogen oxide, m. p. 161° . The reaction probably occurs in accordance with the scheme: $ONPh_2 \cdot N(C_6H_4 \cdot OMe)_2 \rightarrow NPh_2 \cdot N(O)(C_6H_4 \cdot OMe)_2 \rightarrow NPh_2 + O \cdot N(C_6H_4 \cdot OMe)_2$.

Attempts to prepare the hydroxylamine, $NMe_2 \cdot C_6H_4 \cdot NPh \cdot OH$, did not lead to the desired result, since the bulk of the *p*-nitrosodimethylaniline was recovered unchanged after the action of magnesium phenyl bromide on this substance; *pp'*-azodimethylaniline, m. p. 263° , was also produced in small amount.

N-Phenyl-*N*-*p*-tolylhydroxylamine, $C_6H_4Me \cdot NPh \cdot OH$, colourless, lustrous needles, m. p. 65–66° (decomp.), is prepared by the action of magnesium phenyl bromide on nitrosotoluene. It is reduced by tin and hydrochloric acid to phenyl-*p*-tolylamine. Phenyl-*p*-tolyl-nitrogen oxide appears to be formed when an absolute ethereal solution of the hydroxylamine is treated with silver oxide and ignited sodium sulphate at -5° ; the garnet-red crystals are, however, so unstable that they could not be analysed.

Attempts have been made to apply the reactions characteristic of diarylnitrogen oxides to sodium nitrosodisulphonate (Fremy's salt), $(SO_3Na)_2N \cdot O$, which appears to contain quadrivalent nitrogen. Its solution in water is rapidly decolorised by nitric oxide with formation of nitrous acid: $O:N(SO_3Na)_2 \cdot N \cdot O \longrightarrow X(SO_3Na)_2 \cdot OH + HO \cdot NO$, but reaction only occurs in the presence of a trace of acid. Fremy's salt is reduced by phenylhydrazine to nitrogen (evolved from the hydrazine) and hydroxylamine disulphonate.

p-Nitroso-*N*-diphenylhydroxylamine cannot be dehydrogenated to the corresponding diarylnitrogen oxide; since inhibition is not caused by the presence of the nitroso-group, it is probable that the substance has the constitution $OH \cdot N \cdot C_6H_4 \cdot NPh \cdot O$ instead of the usually accepted $NO \cdot C_6H_4 \cdot NPh \cdot OH$. H. W.

Naphthalenesulphonic Acids. IV. Solubilities of some Amine Salts of Naphthalenesulphonic Acids. H. WALES (*J. Ind. Eng. Chem.*, 1922, **14**, 317–318).—The solubilities of salts formed by different naphthalenesulphonic acids with α - and β -naphthylamine were investigated. As hydrolysis occurs in some cases with water, *N*/100-hydrochloric acid was used as solvent, the acid of this strength having no influence on the solubility. Of the disulphonates, the 1 : 5- α -naphthylamine salt, and the 2 : 6- β -naphthylamine salt are least soluble. As a general rule, the more symmetrical a salt, the lower is its solubility. The solubility curve of α -naphthylamine naphthalene- β -sulphonate shows an allotropic change at 54°, and that of the corresponding α -sulphonate at 66°. A complete series of solubilities as determined between 25° and 98° is tabulated. C. I.

Catalytic Hydrogenations under Pressure in the Presence of Nickel Salts. I. Indene and Acenaphthene. JULIUS

VON BRAUN and GEORG KIRSCHBAUM (*Ber.*, 1922, **55**, [B], 1680–1686).—The method adopted is essentially that due to Schroeter (this vol. i, 122), hydrogenation being effected under a pressure of 10–15 atmospheres at a suitable temperature in an autoclave provided with stirring gear and in the presence of a nickel catalyst. At 200°, indene is very readily transformed into hydrindene, b. p. 176°, the yields being theoretical. At 210°, technical acenaphthene which has been purified by a single crystallisation from alcohol is rapidly and quantitatively reduced to tetrahydroacenaphthene [tetraphthene], b. p. 115°/12 mm. The latter hydrocarbon is dis-

tinguished from hydrindene and tetrahydronaphthalene by its ready susceptibility to oxidising agents. Whereas it is stable when preserved in closed vessels and becomes coloured merely pale yellow by exposure to air, it behaves towards permanganate as an unsaturated compound. For this reason, its smooth nitration has not yet been accomplished. Tetrahydroacenaphthene is converted by acetyl chloride and aluminium chloride in the presence of carbon disulphide into 5-acetyltetrahydroacenaphthene, a colourless liquid, b. p. 180—181°/13 mm., which is oxidised by dilute nitric acid to benzene-1 : 2 : 3 : 4-tetracarboxylic acid. The conclusive proof that the acetyl group enters the molecule in position 5 is deduced from a study of its dehydrogenation (von Braun, Hahn, and Seemann, following abstract). The compound gives a *semicarbazone*, m. p. 240—241°, and an *oxime*, m. p. 148°.

The treatment of tetrahydroacenaphthene with sulphuric acid at temperatures between 0° and 80° or higher leads mainly to the production of tetrahydroacenaphthene-4-sulphonic acid, leaflets, m. p. 104—105°; the sodium, calcium, and lead salts are described. The corresponding chloride, glassy needles, m. p. 69—70°, amide, m. p. 154°, and anilide, m. p. 170°, are described. Reduction of the sulphonyl chloride by zinc dust in the presence of ether leads to the formation of tetrahydroacenaphthene-4-sulphinic acid, cubes, m. p. 102—103°. Zinc dust and sulphuric acid reduce the sulphonyl chloride to 4-thioltetrahydroacenaphthene, b. p. 167—169°/12 mm.; the corresponding methyl ether, b. p. 180—182°/10 mm., and disulphide, m. p. 129°, are described. Sodium tetrahydroacenaphthene-4-sulphonate is transformed with some difficulty and in poor yield by molten potassium hydroxide into 4-hydroxytetrahydroacenaphthene, m. p. 98—99°.

H. W.

Benzopolymethylene Compounds. III. Dehydrogenation of Tetrahydronaphthalene, Hydrindene and Tetrahydroacenaphthene [Tetraphthene] Derivatives. JULIUS VON BRAUN, ERICH HAHN and JON SEEMANN (*Ber.*, 1922, **55**, [B], 1687—1700).—

The processes of substitution in the aromatic portion of tetrahydronaphthalene and of naphthalene follow different laws. In the former case, nitration, bromination, chlorination, etc., lead to a mixture of α - and β -derivatives which frequently are readily separable from one another, whereas α -derivatives are formed from naphthalene, and the corresponding β -compounds can often only be prepared by circuitous methods. Since, however, tetrahydronaphthalene is readily re-converted into naphthalene, it appeared possible that a ready method of preparing otherwise difficultly accessible naphthalene compounds might be opened up through the tetrahydro-compounds. In a number of cases it is now shown that the dehydrogenation of the tetrahydronaphthalene derivatives can be effected smoothly. Unfortunately, a similar process does not appear to be applicable to hydrindene and its derivatives, since these substances are unaffected by mild treatment and the

molecule is extensively decomposed in circumstances which are sufficiently drastic to induce reaction. On the other hand, tetrahydroacenaphthene is readily dehydrogenated, yielding, according to circumstances, acenaphthene or acenaphthylene.

β -Ethyltetrahydronaphthalene is decomposed when distilled in an atmosphere of carbon dioxide through a tube (empty or filled with pumice coated with lead oxide) at 650° into β -ethylnaphthalene, b. p. $251-252^{\circ}$ /atmospheric pressure; at 606° very little action occurs, whereas at 700° the ethyl group is also eliminated and naphthalene is formed. Similar observations are made with β -tetrahydronaphthyl methyl ketone, the optimum temperature for the conversion of which into β -naphthyl methyl ketone is $680-700^{\circ}$. The pure ketone has m. p. $53-54^{\circ}$ and gives an *oxime*, m. p. $143-144^{\circ}$, a *semicarbazone*, m. p. 230° , and a *phenylhydrazone*, m. p. $176-177^{\circ}$.

Tetrahydronaphthyl methyl ketone condenses with isation in boiling aqueous alcoholic, alkaline solution with the formation of 2- β -tetrahydronaphthyleinchronic acid, m. p. $198-199^{\circ}$ (decomp.) [the sodium and copper salts and the ethyl ester, needles, m. p. 86° , are described]. When heated until carbon dioxide ceases to be evolved, the acid is converted into 2- β -tetrahydronaphthylquinoline, needles, m. p. 75° (*picrate*, m. p. 191° ; *hydrochloride*, m. p. 227° ; *methiodide*, m. p. 190°). The base is dehydrogenated by lead oxide-pumice at 700° with formation in more than 50% yield of 2- β -naphthylquinoline, m. p. 161° (*methiodide*, orange-coloured prisms, m. p. 188°).

Tetrahydroacenaphthene is almost quantitatively transformed by sulphur at 180° into acenaphthene; under similar conditions, the acetyl group of acetyltetrahydroacenaphthene is also affected. If, however, the latter is heated at 700° , a large amount of acenaphthylene is produced together with smaller quantities of incompletely dehydrogenated acetyltetrahydroacenaphthene from which 5-acetylacenaphthene can be isolated in the form of its semicarbazone.

β -Nitrotetrahydronaphthalene suffers a complicated decomposition when heated at a high temperature. On the other hand, it reacts readily with bromine at 100° , giving a *dibromonitrotetrahydronaphthalene* which could not be caused to crystallise; the latter substance evolves hydrogen bromide at a somewhat higher temperature, giving β -nitronaphthalene, m. p. 79° , the yield being 96-98% of that theoretically possible. The process appears to be the best method favourable at present for the preparation of β -nitronaphthalene when the pure tetrahydro-derivative is available. Unfortunately, although the nitration of tetrahydronaphthalene is a simple operation, the separation of the α - and β -isomerides is somewhat tedious. α -Nitrotetrahydronaphthalene is smoothly dehydrogenated in the same manner as the β -compound. If, however, the process is applied to the mixed tetrahydro-compounds a mixture of nitronaphthalenes is produced which cannot be separated by distillation or by crystallisation from alcohol.

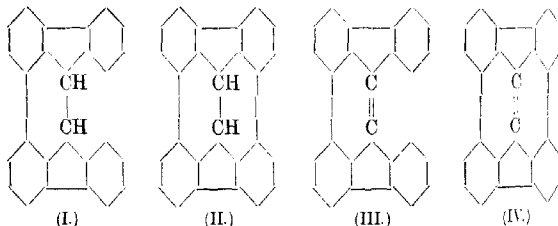
β -Nitronaphthalene is readily brominated with the formation of 5 (or 8)-bromo-2-nitronaphthalene, needles, m. p. 131° , which is reduced by stannous chloride to 5 (or 8)-bromo-2-aminonaphthalene, colourless crystals, m. p. 35° , b. p. $207-210^\circ/16$ mm.; the corresponding *picrate*, needles, m. p. 216° ; *hydrochloride*, m. p. 265° after darkening at 230° ; *acetyl* compound, m. p. 158° ; *benzoyl* compound, m. p. 109° , and *benzylidene* derivative, m. p. 63° , are described. The amine is converted in the usual manner into 5 (or 8)-bromo-2-hydroxynaphthalene, colourless needles, m. p. 105° , but the yields are only moderate owing to the simultaneous production of the compound, $C_{10}H_6Br \cdot N \cdot N \cdot C_{10}H_5Br \cdot NH_2$, cinnabar red needles, m. p. 115° . The naphthal is oxidised by permanganate to 3-bromophthalic acid.

H. W.

The Pyrogenic Transformation of Fluorene. K. DZIEWOŃSKI and J. SUSZKO (*Roczniki Chemji*, 1921, 1, 387—410).—Fluorene vapour is passed under reduced pressure, through a quartz tube, heated to redness, and containing a coil of iron wire. The vapours condense to an oily solid, mainly unchanged fluorene, but containing three other hydrocarbons, of the empirical formulae $C_{26}H_{18}$, $C_{26}H_{14}$, and $C_{26}H_{12}$. Graeber (A., 1893, i, 38) obtained a substance, $C_{26}H_{16}$, by passing fluorene vapours over heated lead oxide, but this substance, biphenylene-ethylene, is shown to be different from the substance of the same empirical formula obtained by the author.

This hydrocarbon, *difluorenylene* (formula I) forms colourless prisms, m. p. 218° , and is identical with the hydrocarbon, $C_{26}H_{16}$, obtained by Klinges and Lonnes (A., 1896, i, 691) from tetraphenyl-epinacolin, to which an asymmetrical structure was wrongly assigned. The *picrate*, reddish-brown needles, m. p. $202-203^\circ$, the *dinitro*-derivative, m. p. $360-365^\circ$ (decomposition), and *dihydroxy*-derivative, colourless, rhombic plates, m. p. 269° , were prepared.

The second hydrocarbon, *dihydrorubicene*, $C_{26}H_{14}$ (formula II), forming colourless needles, m. p. 296° , is obtained in small quantity only. The *picrate*, orange needles, m. p. $254-260^\circ$, is unstable. The



third product, rubicene, $C_{26}H_{12}$, forms deep red needles, m. p. 305° , and seems to be best prepared by this method. Pummerer (A., 1912, i, 182), who prepared it from phenanthraquinone, assigned to it the empirical formula $C_{26}H_{14}$ and the structure III; this is shown to be incorrect, and the structure IV is assigned to it. The *picrate*,

reddish-brown needles, m. p. 258° , is unstable; the *dinitro*-derivative, brick-red needles, m. p. $440-442^{\circ}$ (decomp.), and the *dibromo*-derivative, brownish-red needles, m. p. 378° (decomp.), were prepared, also a *rubicenedisulphonic acid*, which is found to act as an acid dye. Attempts to reduce the hydrocarbon did not lead to any definite results, whilst oxidation with chromic acid mixture gives a yield of only 5% yellow plates, m. p. 203° , and of a feebly acid nature. R. T.

Aniline Arsenates. E. PATERNO (*Atti R. Accad. Lincei*, 1922, [v], 31, i, 165-169).—According to Béchamp, aniline forms a dianiline arsenate, m. p. 140° , which loses aniline at 180° , giving a monoaniline arsenate. The author finds that the former salt, which forms trimetric crystals, is always obtained when aniline is treated in the cold with aqueous arsenic acid. When distilled either in a vacuum at 60° or in a current of steam, or when left in a desiccator over sulphuric acid, the dianiline salt loses aniline, giving the monoaniline salt, which forms vitreous prisms, m. p. 154° , belonging to the triclinic system; if the fused salt is allowed to solidify, it then melts at a somewhat lower temperature. The melting point of the dianiline salt varies for different samples and different modes of heating, from about 140° to about 150° , and cannot be determined exactly owing to the readiness with which the salt undergoes change. Cryoscopic measurements show that the monoaniline salt is hydrolysed into two, and the dianiline salt into three molecules.

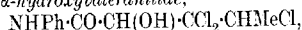
Solutions of aniline in water and of water in aniline have also been investigated cryoscopically. The maximum solubility of aniline in water is about 3.7% at -0.6° and that of water in aniline about 2.8% at -5.4° ; Alexéev (A., 1877, ii, 472) gave for these solubilities at the ordinary temperature 3.11% and 4.58%, respectively, the latter being evidently too high. T. H. P.

The Hydroferrocyanides and Hydroferricyanides of the Organic Bases. I. WILLIAM MURDOCH CUMMING (T., 1922, 121, 1287-1298).

isoNitriles. III. **Reactions with the Hydrates of Halogenated Aldehydes.** M. PASSERINI (*Gazzetta*, 1922, 52, i, 432-435).—The results previously obtained (A., 1921, i, 895) suggest that, in the reaction of an *isonitrile* with an aldehyde or a ketone in presence of an organic acid, the aldehyde or ketone first forms with the organic compound a labile additive compound of the structure, $\text{OH}\cdot\text{CR}_2\cdot\text{O}\cdot\text{CO}\cdot\text{R}$, capable of reacting with *isonitrile* groups. The accuracy of this suggestion is supported by the fact that the analogous compounds formed by halogenated aldehydes with water, $\text{OH}\cdot\text{CHR}\cdot\text{OH}$, react with phenylcarbylamines yielding anilides of halogenated α -hydroxy-acids, $\text{R}\cdot\text{N}\cdot\text{C}+\text{OH}\cdot\text{CHR}\cdot\text{OH}=\text{NHR}\cdot\text{CO}\cdot\text{CHR}\cdot\text{OH}$. Thus, chloral hydrate and phenylcarbylamine yield β -trichloro- α -lactanilide, and butylchloral hydrate and phenylcarbylamine, $\beta\beta\gamma$ -trichloro- α -valeranilide.

β -Trichloro- α -lactanilide, $\text{NPh}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$, crystallises in colourless, elongated plates or flat needles, m. p. 147° , and is readily decomposed by alkali hydroxide or carbonate with quantitative loss of the chlorine. It is highly resistant towards the action of acids, but is converted into trichlorolactic acid when heated with excess of hydrochloric acid in a sealed tube at 80 — 100° . The compound, m. p. 164 — 165° (decomp.), described as trichlorolactanilide and obtained by Anschütz and Haslam (A., 1890, 27) from aniline and tetrachloroethylidene trichlorolactate, may be an isomeride of the above compound.

$\beta\beta\gamma$ -Trichloro- α -hydroxyvaleranilide,



forms colourless, highly refractive plates, m. p. 156 — 158° , and yields aniline and $\beta\beta\gamma$ -trichloro- α -hydroxyvaleric acid when heated in a sealed tube with hydrochloric acid.

T. H. P.

Akylation of Amines with Sulphonic Esters. ZOLTAN FÖLDI (Ber., 1922, 55, [B], 1535—1543).—The reaction between sulphonic esters and amines does not proceed more uniformly than that between amines and alkyl haloids. Quaternary salts are, however, obtained smoothly and quantitatively as the sole final product of the action of sulphonic esters on tertiary amines. Primary and secondary amines, on the other hand, give more or less uniform results. The process does not stop at the stage indicated by the equation $\text{Ph}\cdot\text{SO}_2\text{Me} + \text{NH}_2\text{Ph} = \text{NHMePh}\cdot\text{Ph}\cdot\text{SO}_3\text{H}$, since the secondary base is partly displaced from its salt by unchanged primary amine (even when the latter is the relatively weaker) and then suffers further alkylation. The process is explained by the reversibility of the change $\text{NHMePh}\cdot\text{SO}_3\text{HPh} + \text{NH}_2\text{Ph} \rightleftharpoons \text{NH}_2\text{Ph}\cdot\text{SO}_3\text{HPh} + \text{NHMePh}$. This disadvantage can be remedied to some extent by using an excess of the initial amine, but this procedure suffers from the defect that it causes a displacement of the equilibrium in an unfavourable sense. The reactivity of phenols towards sulphonic esters has been found to diminish with increasing acidity of the phenolic hydroxy-groups. A definite relationship between reactivity and basicity, however, does not appear to exist in the case of amines, since the feebly basic and usually slightly reactive diphenylamine is attacked by sulphonic esters with the same vigour as methylaniline or aniline.

The following substances do not appear to have been described previously: allyl-*p*-toluidine, b. p. 122 — $125^\circ/12$ mm.; diallylanthranilic acid, transparent rhombohedra, m. p. 86° ; phenyltrimethylammonium toluene-*p*-sulphonate, colourless, very hygroscopic crystals, m. p. 159° ; diphenylmethylamine ferrocyanide, $\text{C}_{13}\text{H}_{13}\text{N}\cdot 2\text{H}_2\text{FeC}_6\text{N}_6$, colourless, somewhat unstable needles; diphenylallylamine, a colourless liquid which rapidly becomes purplish-red, b. p. 185 — $190^\circ/12$ mm., about 320 — 325° (decomp.) /atmospheric pressure; 1-methylpyridinium toluene-*p*-sulphonate, unusually hygroscopic crystals, m. p. 136 — 137° ; 1-allylpyridinium benzenesulphonate, very hygroscopic crystals; N-methylpapaverinium toluene-*p*-sulphonate, m. p.

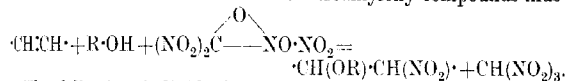
171°; *N*-allylpapaverinium benzenesulphonate, m. p. 174—175°, pale yellow needles (+2H₂O), lemon-yellow rods (anhydrous); *N*-allylbrucinium benzenesulphonate (anhydrous and trihydrate), m. p. 148—150°, slight decomp. 150—160° and m. p. 238° after re-solidification; benzenesulphonyldiallylamine, a pale yellow, viscous liquid, b. p. 180—190°/11 mm., d_4^{25} 1.086.

Sulphonic esters can be used for the preparation of nitriles, since they react as easily as the alkyl sulphates with potassium cyanide.

H. W.

Reciprocal Induced Polarity Effects in Cresols and their Derivatives. Properties of the Isomeric Methoxybenzyl Bromides. ARTHUR LAPWORTH and JOHN BALDWIN SHOESMITH (T., 1922, 121, 1391—1400).

Tetranitromethane. V. Tetranitromethane as Nitrating Agent. II. ERICH SCHMIDT, RICHARD SCHUMACHER, WILLY BÄREN, and ADALBERT WAGNER (*Ber.*, 1922, 55, [B], 1751—1759; cf. Schmidt and Fischer, A., 1920, i, 726, 727).—It has been shown previously (*loc. cit.*) that tetranitromethane in the presence of pyridine can effect the replacement of hydrogen attached to carbon atoms united by an olefinic double bond by the nitro-group. The entrance of the nitro-group, however, depends on the position of the double bond relatively to the aromatic nucleus. Allyl compounds (*o*-esdragole, safrole, eugenyl methyl ether, myristicin, and apiole) are unaffected, whereas the isomeric propenyl derivatives are transformed into the corresponding β -nitro-compounds. Unsaturated compounds which are nitrated by tetranitromethane and pyridine with retention of the double bond are converted by tetranitromethane and alcohols into nitroalkoxy-compounds thus:



The following individual substances are described: β -nitro-*o*-anethole, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CMe}\cdot\text{NO}_2$, m. p. 52—53°, b. p. 127—128°/0.5 mm.; β -nitroisoeugenyl methyl ether, m. p. 72°; β -nitroasarone, $\text{C}_6\text{H}_5(\text{OMe})_2\cdot\text{CH}\cdot\text{CMe}\cdot\text{NO}_2$, m. p. 98—99°; β -nitroisomyristicin, $(\text{H}_2\text{O})_2\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}\cdot\text{CMe}\cdot\text{NO}_2$, m. p. 111—112°; β -nitroisopiole, $\text{CH}_3\text{O}_2\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CH}\cdot\text{CMe}\cdot\text{NO}_2$, yellow needles, m. p. 110—111°.

The following compounds are obtained by the gradual addition of an alcoholic solution of tetranitromethane to a boiling solution of the unsaturated substance in alcohol; the solution is poured into water and extracted with ether. The ethereal solution is decolorised and treated for some time with an aqueous suspension of magnesium oxide: β -nitro- α -methoxydihydro-*p*-anethole, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OMe})\cdot\text{CHMe}\cdot\text{NO}_2$, m. p. 49—50°, b. p. 133—135°/0.5 mm.; β -nitro- α -methoxydihydro-*o*-anethole, needles, m. p. 63—64°, b. p. 127—128°/0.5 mm.; β -nitro- α -ethoxydihydro-*p*-anethole, a pale yellow liquid, b. p. 137°/0.5 mm.; β -nitro- α -ethoxydihydro-*o*-anethole, a pale yellow liquid, b. p. 125°/0.5 mm.; β -nitro- α -methoxydihydro-

isosafole, $\text{CH}_3\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}(\text{OMe})\cdot\text{CHMe}\cdot\text{NO}_2$, colourless crystals, m. p. 67—68°, b. p. 138—140°/0.5 mm.

p-Nitrodimethylaniline is converted by tetranitromethane, glacial acetic acid, and alcohol into methyl-*p*-nitrophenylnitrosamine, m. p. 100—101°. Similarly, *p*-dimethylaminobenzonitrile gives *p*-methylnitrosoaminobenzonitrile, colourless crystals, m. p. 125°, and 2:4-dinitrodiethylaniline is transformed into 2:4-dinitroethylaniline, m. p. 113—114°. H. W.

Decomposition of Benzyl Disulphoxide. JOHN ARMSTRONG SMYTHE (T., 1922, 121, 1400—1405).

Organomagnesium Derivatives. A. GARCÍA BANÚS and J. PASCUAL VILA (*Anal. Fis. Quim.*, 1921, 19, 326—346; cf. Smidlin and García Banús, A., 1913, i, 50).—The reaction of Grignard reagents with certain aldehydes and ketones and in particular with benzaldehyde, is discussed with reference to the possibility that these organomagnesium compounds exist in two tautomeric forms, one of which is supposed to possess two active radicles and to be able to condense with two molecules of an aldehyde or ketone. Magnesium benzyl chloride, however, reacts normally with benzophenone and benzil; In the experimental portion, the reaction of magnesium benzyl chloride with benzil is studied. Equimolecular proportions of these compounds in ethereal solution give *benzoylphenylbenzylcarbinol* (benzylbenzoin), $\text{CH}_2\text{Ph}\cdot\text{CPhBz}\cdot\text{OH}$, obtained after recrystallisation in white needles, m. p. 120—121°. The crystals are triclinic. It gives a *syn-oxime*, m. p. 175—176°. The *phenylhydrazone* forms colourless crystals m. p. 115—116°, after softening at 61—62°. From the products of the reaction of one molecule of benzil with two molecules of magnesium benzyl chloride α - and β -*deoxybenzoinpinacones*, $\text{CH}_2\text{Ph}\cdot\text{CPh}(\text{OH})\cdot\text{CPh}(\text{OH})\cdot\text{CH}_2\text{Ph}$, are obtained. The α -pinacone forms white prisms, m. p. 215—216°. They are rhombic tetragonaloid; $a:b:c = 0.8746:1:0.7514$ (?). The β -pinacone has m. p. 172—173° and forms white, monoclinic needles; $a:c = 1:0.2475$; $\beta = 92^\circ 7'$. By varying the conditions of reaction dibenzyl may be obtained. G. W. R.

Condensations of *p*-Nitrobenzyl Chloride with Cinnamaldehyde and Furfuraldehydes. ERNST KLEUCKER (*Ber.*, 1922, 55, [B], 1634—1634).—A solution of *p*-nitrobenzyl chloride in methyl alcohol is converted by cinnamaldehyde and potassium carbonate at 35—40° into a mixture of *cis*- and *trans*- α -phenyl-

δ -*p*-nitrophenyl- $\Delta^{\alpha\gamma}$ -butadiene oxide, $\text{O} \begin{array}{c} \diagup \text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 \\ | \\ \diagdown \text{CH}\cdot\text{CH}\cdot\text{CHPh} \end{array}$, which are

separated by taking advantage of the readiness with which the *cis*-variety forms supersaturated solutions in alcohol. The *cis*- and *trans*-modifications have m. p. 115° and 148°, respectively. [*p*-Nitrobenzyl chloride is converted by potassium carbonate and methyl alcohol into 4:4'-dinitrostilbene and *p*-nitrobenzyl methyl

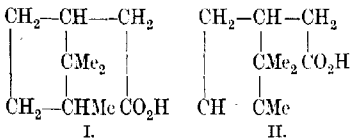
ether, m. p. 26—27°]. The *trans*-variety is oxidised by potassium permanganate in the presence of acetone to benzoic acid and *p*-nitrophenylglycidic acid, m. p. 186—188° (decomp.), the identity of the latter being confirmed by converting it by means of concentrated hydrochloric acid into β -chloro-*p*-nitrophenylpropionic acid, m. p. 167—168°. The similar oxidation of the *cis*-acid gives benzoic and *cis*-*p*-nitrophenylglycidic acid, m. p. 124—125°, which is converted by concentrated hydrochloric acid into *cis*-3(?)*-chloro-p*-nitrophenylpropionic acid, m. p. 125—126°. Either of the α -phenyl- δ -*p*-nitrophenyl- $\Delta^{\alpha\gamma}$ -butadiene oxides, when suspended in anhydrous ether and treated with dry hydrogen chloride, yields a mixture of *cis*- and *trans*- α -phenyl- δ -*p*-nitrophenyl- $\Delta^{\alpha\gamma}$ -butadiene- $\gamma\alpha$ -chlorohydrins, $\text{NO}_2\text{C}_6\text{H}_4\text{CHCl}\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{CHPh}$, m. p. 105—110°, which is converted by boiling glacial acetic acid into (?) *p*-nitrobenzyl styryl ketone, m. p. 144° (the corresponding *oxime*, m. p. 121—122°, could not be obtained in a perfectly homogeneous condition).

In a similar manner, *p*-nitrobenzyl chloride and furfuraldehyde give *trans*-*p*-nitrophenyl-2-furylethylene oxide, colourless crystals, m. p. 117°, and *cis*-*p*-nitrophenyl- α -furylethylene oxide, colourless needles, m. p. about 85°. Either variety is converted by hydrogen chloride and ethyl alcohol into ethyl δ -*p*-nitrobenzylidenelævulate, $\text{NO}_2\text{C}_6\text{H}_4\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, m. p. 107°. The corresponding methyl ester has m. p. 150°. Hydrolysis of the ester by boiling glacial acetic acid containing a little concentrated sulphuric acid leads to the production of δ -*p*-nitrobenzylidenelævulic acid, m. p. 169°, which is oxidised by potassium permanganate to *p*-nitrobenzoic and succinic acids. The acid may also be prepared by the condensation of *p*-nitrobenzaldehyde with lævulic acid; the corresponding semicarbazone has m. p. about 210°. Ethyl δ -*p*-nitrobenzylidenelævulate gives two semicarbazones, $\text{C}_{15}\text{H}_{18}\text{O}_5\text{N}_4$, m. p. 207—209° and 175—180°, respectively. If a solution of *cis*- or *trans*-*p*-nitrobenzyl- α -furylethylene oxide in hot ethyl or methyl alcohol is poured into boiling water, *p*-nitrobenzyl α -furyl ketone (?), pale yellow, prismatic crystals, m. p. 158—159°, is produced (the corresponding *oxime*, m. p. 136—138°, could not be obtained in the homogeneous condition). The ketone is oxidised by hydrogen peroxide in alcoholic alkaline solution to *p*-nitrobenzoic and pyromucic acids.

H. W.

Comparison of α -Campholanic Acid with Mahla and Tiemann's Dihydrocampholenic Acid and with *iso*-Campholic Acid. P. LIEF (*Ber.*, 1922, 55, [B], 1883—1892).—

Dihydrocampholenic acid (formula I) has been isolated by Mahla and Tiemann (*A.*, 1900, i, 507) by a peculiar transformation of camphorimine, and its constitution has been deduced from its oxidative degradation. If the formula



assigned to it is correct, it must be produced by the hydrogenation-

tion of α -campholenic acid (formula II), but according to van Kregten (*Diss.*, Gröningen. 1910), this does not appear to be the case when the Sabatier-Senderens method is used. The author considers that the question can only be elucidated satisfactorily by a study of the optically inactive compound. He has therefore converted *dl*-camphor into *dl*-dihydrocampholenic acid on the one hand and into *dl*- α -campholenic acid on the other; the latter acid is hydrogenated by Skita's method in acid and alkaline or neutral medium, thereby yielding *trans*- and *cis*- α -campholanic acids, the former of which is identical with the *dl*-acid prepared according to Mahla and Tiemann.

Fission of the camphor ring with alkali leads to the formation of campholic acid, together with a small proportion of *isocampholic* acid. It has been suggested, without experimental evidence being adduced, that the latter acid is identical with α -campholanic acid (Mahla and Tiemann, *loc. cit.*). A comparison of *dl*-*isocampholic* and *dl*- α -campholanic acids shows that the substances are closely similar to, but certainly not identical with, one another. The supposed marked difference in strength between campholic and *isocampholic* acids does not exist.

dl-Camphoroxime is converted, according to Tiemann's method (*loc. cit.*), into *dl*- α -campholenic acid, b. p. 148.2°—149.2° (corr.)/15 mm. (amide, m. p. 115°—116°), which is hydrogenated in ethereal solution in the presence of spongy platinum to *dl*-*cis*- α -campholanic acid, b. p. 150.9—151.2° (corr.)/14 mm. [chloride, b. p. 102°—104°/16 mm., amide, lustrous leaflets, m. p. 129—130° (corr.); anilide, prismatic crystals, m. p. 140—141°]. The *cis*-acid is also obtained by the catalytic hydrogenation of α -campholenic acid, according to Sabatier-Senderens, in the presence of nickel as catalyst at 200°. On the other hand, treatment of α -campholenamide in ethereal methyl alcoholic solution with hydrogen in the presence of spongy platinum gives *trans*- α -campholanamide, rectangular leaflets, m. p. 124.5—125° (corr.). *dl*-Camphoroxime is converted successively in accordance with the procedure of Mahla and Tiemann (*loc. cit.*) into *dl*-camphorimine nitrite, decomp. 160°, *dl*-dihydrocampholenonitrile, b. p. 112—117°/16 mm., and *dl*-dihydrocampholenic acid, which is identified with *trans*- α -campholanic acid [anilide, m. p. 136—137° (corr.)].

The following derivatives of *dl*-*isocampholic* acid are described: chloride, b. p. 88—89° (corr.)/10 mm.; amide, m. p. 109—110° (corr.); anilide, m. p. 137—139° after previous softening.

H. W.

The Spontaneous Decomposition of Imino-ethers.

TREAT B. JOHNSON and LAWRENCE W. BASS (*J. Amer. Chem. Soc.*, 1922, **44**, 1341—1343).—Samples of carefully purified benzonitrile, benziminomethyl ether, benziminoethyl ether, benziminoisobutyl ether, and *p*-toluiminomethyl ether were kept for twenty-two years in sealed glass vessels and then examined. In every case, with the exception of benzonitrile, heavy, crystalline deposits of cyapherine

combinations and also unaltered nitrile were found, the amount of dissociation and polymerisation varying with the ether. The pure benzonitrile showed no evidence of polymerisation. W. G.

The Formation of Salts from Aromatic Nitro-compounds. I. LIFSCHITZ (*Ber.*, 1922, **55**, [B], 1631—1634).—Isomeric salts and esters from *p*-nitrophenylacetonitrile have been described by Jenner and Lifschitz (*A.*, 1916, i, 45), who have ascribed to them a paraquinonoid structure. Their observations have been confirmed by Opolski, Kowalski, and Pilewski (*A.*, 1917, i, 25), who also claim to have isolated similar compounds from *m*-nitrophenylacetonitrile, which they regard as having a meta-quinonoid structure. Repetition of the latter work with carefully purified *m*-nitrophenylacetonitrile has not given evidence of the formation of such compounds. The spectrum of an absolute alcoholic solution of *m*-nitrophenylacetonitrile which has been treated with sodium ethoxide does not contain any characteristic bands and is not in any way analogous to that of the para-salts. These solutions are very unstable, so that even with rapid work distinct changes in absorption occur during the exposures. Recovery of the paranitrile from such solutions appears to be impossible. The preparation of the solid salts by means of ethereal sodium ethoxide could not be effected.

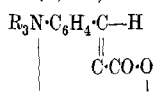
H. W.

The Addition of Bromine to the *trans*-Substituted Cinnamic Acids. C. F. VAN DUTN (*Rec. trav. chim.*, 1922, **41**, 402—418).—Measurements of the velocity of the reaction, in presence of different concentrations of hydrochloric acid, between bromine and the $\text{R}\begin{smallmatrix} \diagup \text{CO-OH} \\ \diagdown \text{SO}_3 \end{smallmatrix}$ and $\text{R}\begin{smallmatrix} \diagup \text{CO-O}^+ \\ \diagdown \text{SO}_3^- \end{smallmatrix}$ ions have been made, the latter being derived from the normal and acid sodium salts of the three sulphocinnamic acids. The results show that the reaction is of the bimolecular type and that the differences in the constants depend entirely on differences in the speed of reaction of the ions. Negative catalysis due to the presence of hydrogen ions does not occur. The small variations which are found in the constant for the reaction are attributed to the comparatively large changes in the concentration of the hydrochloric acid. The reaction velocities in the case of the normal sodium salts are so great that it is only towards the end of the reaction that measurements are practicable; this involves considerable experimental error, so that the resulting figures are of value only from a comparative point of view. The rate at which the addition of bromine takes place, in the case of both ions, is greatest for the meta- and least for the para-compound; but the influence of the position of the sulphonic group is only of secondary importance compared with the retarding action exerted by that group. This is shown by comparing the results obtained by Barrett and Lapworth (*T.*, 1908, **93**, 85) for cinnamic acid, $K > 1000$, with the values (29 to 52) obtained for the sulphocinnamic acids.

H. J. E.

Betaines. II. Betaines of the Cinnamic Acid Series.

PAUL PFEIFFER and GERHARD HAEFELIN (*Ber.*, 1922, 55, [B], 1769—1788).—Theoretical considerations have led the author (this vol., i, 720) to advance the formula, ${}^+\text{NMe}_3\text{—R—}^-\text{CO—O}^-$, for the



betaines. An opportunity of testing its validity lies in the preparation of betaines of the *trans*-cinnamic acid series, since, according to the older methods of formulation (annexed formula) these substances cannot be conceived as capable of existence. Such betaines are found to be readily prepared.

Methyl trans-p-dimethylaminocinnamate, pale yellow, lustrous leaflets, m. p. 135—136°, is prepared by the condensation of *p*-dimethylaminobenzaldehyde with methyl acetate in the presence of sodium. It gives a *perchlorate*, colourless, prismatic crystals, m. p. 169—170°. It is hydrolysed by concentrated hydrochloric acid to *trans-p*-dimethylaminocinnamic acid, m. p. 220° (*perchlorate*, colourless prisms, m. p. 196—197°). *Ethyl trans-p-dimethylaminocinnamate*, prepared by esterification of the acid with ethyl alcohol and hydrogen chloride but apparently not obtainable from *p*-dimethylaminobenzaldehyde and ethyl acetate, crystallises in pale yellow leaflets, m. p. 76—78°. The methyl ester is converted by methyl iodide into *methyl trans-p-dimethylaminocinnamate methiodide*, pale yellow leaflets, m. p. 174—176° when slowly, 186° when rapidly, heated. An aqueous solution of the latter is converted by moist silver oxide into *trans-p-aminocinnamic acid trimethylbetaine*.

${}^+\text{NMe}_3\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{array}{c} \text{—H} \\ \parallel \\ \text{H}\cdot\text{C}\cdot\text{COO}\text{—} \end{array}$ (annexed formula), colourless, lustrous leaflets, decomp. 214—220°. The substance contains half a molecular proportion of water of crystallisation which cannot be removed without decomposing the betaine. The *hydrochloride*, $[\text{NMe}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}]\text{Cl}$, colourless leaflets, m. p. 240° (decomp.), after darkening at 215° and softening at 210°, the *hydrobromide*, colourless, rhombic crystals, m. p. 225—230° (decomp.) after darkening at 210°, the *iodide* (from *p*-dimethylaminocinnamic acid and methyl iodide or from the betaine and hydriodic acid), pale yellow crystals, m. p. 190—191°, and the *perchlorate*, colourless, lustrous needles, are described.

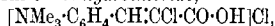
The stereochemical configuration of the dimethylaminocinnamic acid is established in the following manner. *trans*-Cinnamic acid is nitrated to *trans-p-nitrocinnamic acid*, m. p. 286°, which is also obtained by the condensation of *p*-nitrobenzaldehyde with anhydrous sodium acetate in the presence of acetic anhydride. The nitro-acid is reduced to the amino-acid, which is converted into its methyl ester. The amino-acid is transformed by methyl iodide and sodium hydroxide into *trans-p*-dimethylaminocinnamic acid, m. p. 220°, which is identical with the product obtained from *p*-dimethylaminobenzaldehyde.

The constitution of the betaine just described is somewhat obscured by the presence of water of crystallisation. The following

series of experiments was therefore performed. Methyl *trans*-*p*-dimethylaminocinnamate is converted by bromine into the corresponding dibromide, a viscous, yellow liquid, which is converted by warm glacial acetic acid into methyl *trans*- α -bromo-*p*-dimethylaminocinnamate, m. p. 96°. The ester is converted by hydrochloric acid into *trans*- α -bromo-*p*-dimethylaminocinnamic acid, greenish-yellow leaflets, m. p. 175—176°. The methyl ester, when treated with methyl iodide, gives methyl *trans*- α -bromo-*p*-dimethylaminocinnamate methiodide, pale yellow leaflets, m. p. 171—172°, which is transformed by moist silver oxide into *trans*- α -bromo-*p*-amino-

cinnamic acid trimethylbetaine, $\text{NMe}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CBr} \cdot \text{CO} \cdot \text{O}$, long, colourless needles, m. p. 222° (decomp.) after softening at 218—219°. The corresponding *hydrochloride*, colourless needles, which darken at 205° but do not melt below 250°, and the *hydrobromide*, small, colourless needles which become brown at 190° but do not melt below 250°, are described.

trans- α -Chlorocinnamic acid, m. p. 139° (cf. Sudborough and James, T., 1906, 89, 107), is converted by fuming nitric acid into *trans*- α -chloro-*p*-nitrocinnamic acid, pale yellow needles, m. p. 220—221° (*cis*- α -chlorocinnamic acid gives a nitro-acid, m. p. 152—153°), which is reduced by ferrous sulphate and ammonia to *trans*- α -chloro-*p*-aminocinnamic acid, which becomes brown at 219° but does not melt below 250°; the acid is conveniently characterised by conversion into its methyl ester, pale yellow needles, m. p. 123°; the *hydrochloride* of the acid was analysed. The acid is converted by methyl iodide and sodium hydroxide into the betaine, which is isolated in the form of its *hydrochloride*,



pale yellow needles, which darken at about 170°, soften at about 200°, but do not melt below 250°. The corresponding *perchlorate*, colourless leaflets, which darken between 230° and 240°, soften at 250—255°, but are not completely melted below 280°, is described. The free betaine is prepared by heating an aqueous solution of the purified hydrochloride with silver oxide; it crystallises in colourless needles, m. p. 252—256°, after previous darkening. H. W.

Abietic Acid and certain Metal Abietates. LAWRENCE L. STEELE (*J. Amer. Chem. Soc.*, 1922, 44, 1333—1341).—Abietic acid may be prepared readily by boiling white rosin with 98% acetic acid under a reflux condenser for two hours and then, after filtering the mixture, leaving it overnight. The acid, when recrystallised from 98% acetic acid, has m. p. 161—165°; n_D^{20} 1.510, n_D^{25} 1.578, n_D^{30} 1.618; $[\alpha]_D^{20}$ -80.0°, iodine value (Wijs) 168.5—171.1, acid value 186. A number of abietates were prepared by adding a neutral solution of sodium abietate to an excess of an aqueous solution of a salt of the metal. All the abietates prepared, with the exception of the basic chromium salt, were soluble in benzene. The abietates described are those of lead, manganese, cobalt, nickel, chromium, and iron.

W. G.

A Variety of Wax from Pine Needles and certain Abietic Esters. H. P. KAUFMANN and M. FRIEDEBACH (*Ber.*, 1922, 55, [B], 1508—1517).—The dried residue left after the distillation of pine needles with steam is extracted with ether, benzene, and carbon disulphide, thereby giving a dark green, viscous mass the weight of which does not exceed 8–10% of that of the crude material and varies greatly with the season of the year. The isolation of the wax, m. p. 64–65°, can be effected by repeated crystallisation of the green mixture from alcohol, but the process is considerably complicated by the presence of relatively large amounts of resin derived from the twigs (the complete separation of needles and twigs does not appear to be practicable). It is preferable to extract the residue with cold acetone in which the wax does not dissolve; the residue is distilled under diminished pressure, and the distillate is crystallised repeatedly from ethyl alcohol or acetic acid. The wax is hydrolysed by alcoholic sodium hydroxide solution with unusual difficulty, giving a mixture of cetyl, ceryl, and myricyl alcohols. Stearic, palmitic, and hydroxypalmitic acids are present.

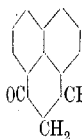
The portion of the crude green wax which is soluble in acetone is a fat-like mass which contains phytosterol, and oleic, stearic, and abietic acids in the form of their esters; the presence of free abietic acid could not be established.

Cetyl abietate, a yellow, waxy mass, m. p. 40°, is prepared by the action of cetyl iodide on silver abietate at 140°. *Myricyl abietate* is a dark brown, brittle substance resembling shellac. H. W.

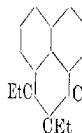
Investigations and Ring Closures in the Series of the Methylnaphthalenes. FRITZ MAYER and ADOLF SIEGLITZ [with E. FISCHER, J. HAGEN, R. JUNG, W. KNIES, C. KOHL, F. LISTVANK, W. NEUGEBAUER and TH. SCHULTE] (*Ber.*, 1922, 55, [B], 1835—1859).—The bromination of α -methylnaphthalene in carbon disulphide solution in the absence of light gives mainly 4-bromo-1-methylnaphthalene, b. p. 162–164°/12 mm. (picrate, m. p. 123–124°), and 4-bromo-1-bromomethylnaphthalene. The position of the bromine atom in the former is established by its conversion into 1-methylnaphthalene-4-carboxylic acid, colourless crystals, m. p. 175° (methyl ester, b. p. 192–194°/12 mm.; ethyl ester, b. p. 203°/12 mm.; chloride, b. p. 150–160°/12 mm.; amide, colourless needles, m. p. 193°; anilide, colourless needles, m. p. 179°). The ethyl ester is transformed through the hydrazide (colourless needles, m. p. 154°) into the urethane, pink needles, m. p. 96°, from which the previously obtained 4-amino-1-methylnaphthalene, m. p. 51°, is derived. 1-Methyl-4-naphthoyl chloride is converted by benzene and aluminium chloride into 4-benzoyl-1-methylnaphthalene, m. p. 174–175°, which is transformed by aluminium chloride at 150° into 4-methylperibenzanthrone, m. p. 115°. 4-Bromo-1-methylnaphthalene is oxidised by dilute nitric acid to 4-bromonaphthalene-1-carboxylic acid, colourless needles, m. p. 212° (methyl ester, colourless needles, m. p. 42°, b. p. 195–200°/15 mm.). The oxidation of 4-methylnaphthalene-1-carboxylic acid by permanganate in alkali

line solution gives *naphthalene-1 : 4-dicarboxylic acid*, colourless rods, m. p. 288° (*methyl ester*, m. p. 64°, b. p. 195—197°/12 mm.).

α -Naphthylmethyl bromide yields $\alpha\beta$ -di-1-naphthylethane, m. p. 161—162°, when treated with magnesium and ether and subsequently with acetaldehyde. It is converted by sodium and ethyl acetoacetate into *ethyl α -1-naphthylmethylacetoacetate*, b. p. 204.5—206°/12 mm., which is transformed by aqueous sodium hydroxide into naphthylpropionic acid and α -1-naphthylbutane- γ -one, b. p. 186—187°/12 mm. (*semicarbazone*, m. p. 176—177°; *oxime*, needles, m. p. 89—91°). Reduction of the ketone with amalgamated zinc and hydrochloric acid gives α -1-naphthylbutane, a colourless, mobile liquid, b. p. 151—152°/14 mm. α -Naphthylmethyl bromide reacts with ethyl malonate and sodium to give *ethyl α -1-naphthylmethylmalonate*, b. p. 221°/11 mm. [An intermediate fraction contains a nuclear brominated methyl-naphthalene, b. p. 161—162°/11 mm. (*picrate*, m. p. 127—128°), which is not identical with 4-bromo-1-methylnaphthalene; on oxidation, it yields small amounts of a *bromonaphthalenecarboxylic acid*, m. p. 215—216°.] The ester is hydrolysed to α -naphthylmethylmalonic acid, m. p. 160—163°, which gives β -1-naphthylpropionic acid, m. p. 151°, when heated. The latter acid is converted by thionyl chloride into the corresponding *chloride*, b. p. 187°/12 mm. (*amide*, leaflets, m. p. 85°), which is transformed by aluminium chloride in the presence of light petroleum into 7 : 8-dihydrophenalene-9* (annexed



formula), yellow leaflets, m. p. 85—86° (*oxime*, m. p. 124—125°). α -Naphthylmethyl bromide and ethyl ethylmalonate yield *ethyl α -1-naphthylmethylmethylmalonate*, b. p. 227°/12 mm., from which α -1-naphthylmethylmethylmalonic acid, needles, m. p. 151—153°, is obtained. The latter loses carbon dioxide at 150—160° and passes into α -1-naphthylmethylbutyric acid, b. p. 223—227°/15 mm. α -1-Naphthylmethylbutyryl chloride, b. p. 188°/12 mm. (corresponding *amide*, m. p. 132°), is transformed by aluminium chloride in the presence of light petroleum into δ -ethyl-7 : 8-dihydrophenalene-9, a viscous, yellow liquid, b. p. 195°/15 mm., which is reduced by amalgamated zinc and hydrochloric acid to δ -ethyl-7 : 8-dihydrophenalene, b. p. 167—168°/16 mm. The phenalene is transformed by magnesium ethyl bromide and distillation into 7 : 8-diethylphenalene (annexed formula), a yellow, odourless liquid, b. p. 185°/13 mm. The latter is oxidised by potassium permanganate to hemimellitic acid.



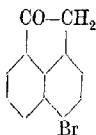
α -Naphthylmethyl bromide and hexamethylenetetramine give an additive compound, colourless needles, m. p. 175—179° (indefinite), which is readily transformed into α -naphthaldehyde, b. p. 150—152°/13 mm. The latter is converted by nitromethane into α -1-

* As the name in use, *perinaphthindanone*, is incorrect (cf. Stelzner, *Lit.-Reg. org. Chem.*, 3, 41, 62) the author suggests that the parent hydrocarbon should be termed "*phenalene*," an abbreviation of the structural name *periphenonaphthalene*.

naphthyl-β-nitroethylene, $C_{10}H_7 \cdot CH \cdot CH \cdot NO_2$, yellow needles, m. p. 87.5° , which is reduced by aluminium amalgam in the presence of ether to *α-naphthylacetaldoxime*, $C_{11}H_7 \cdot CH_2 \cdot CH \cdot N \cdot OH$, colourless needles, m. p. 118° . Treatment of the oxime with sodium amalgam, acetic acid, and alcohol gives *α-naphthylethylamine*, $C_{10}H_7 \cdot CH_2 \cdot CH_2 \cdot NH_2$, b. p. $170-173^\circ/16$ mm. (*hydrochloride*, m. p. $243-248^\circ$; *acetyl derivative*, colourless needles, m. p. 91°). The amine is also prepared from *β-1-naphthylpropionic acid* by successive conversion into the corresponding *hydrazide*, needles, m. p. $125-126^\circ$, *azide*, and *urethane*, colourless, lustrous leaflets, m. p. $50-51^\circ$ and hydrolysis of the latter.

4-Bromo-α-naphthylmethyl bromide, needles, m. p. $103-104^\circ$, is converted by alcoholic sodium ethoxide solution into *4-bromo-α-naphthylmethyl ethyl ether*, b. p. $185-187^\circ/17$ mm.

α-4-Bromonaphthylacetonitrile, needles, m. p. 82° , is hydrolysed to *α-4-bromonaphthylacetic acid*, colourless needles, m. p. $149-150^\circ$. The corresponding *chloride*, a yellow liquid, b. p. $110-112^\circ/12$ mm., and *amide*, colourless needles, m. p. 182° , are described. The chloride is transformed by aluminium chloride in the presence of nitrobenzene into *5-bromoacenaphthenone*, colourless needles, m. p. $174-175^\circ$ (*oxime*, needles, m. p. $215-216^\circ$).



4-Bromo-α-naphthylmethyl bromide reacts with ethyl sodiummalonate to give *ethyl 4-bromo-α-naphthylmethylmalonate*, leaflets, m. p. 55° , b. p. $237^\circ/14$ mm., which is transformed by boiling glacial acetic and hydrochloric acids into *β-4-bromo-α-naphthylpropionic acid*, leaflets, m. p. 148° ; the *chloride* of the latter, b. p. $195^\circ/10$ mm., is converted by aluminium chloride into *7:8-dihydrophenalene-9* (see above).

4-Bromo-α-naphthaldehyde, colourless needles, m. p. 85° , is prepared from *4-bromo-α-naphthylmethyl bromide* and hexamethylenetetramine and is converted by sodium acetate and acetic anhydride at $160-165^\circ$ into *β-4-bromo-α-naphthylacrylic acid*, slender, pale yellow needles, m. p. $250-251^\circ$.

β-4-Methoxy-α-naphthylpropionic acid is transformed successively into the *chloride* and *7:8-dihydrophenalene-9-one*.

1-Bromo-2-methylnaphthalene, b. p. $165-170^\circ/13$ mm., $290-295^\circ/760$ mm. (picrate, m. p. 113°), is converted in the manner described for the *α-series* into *2-methylnaphthalene-1-carboxylic acid*, colourless prisms, m. p. $126-127^\circ$. The acid cannot be esterified with alcohol and hydrogen chloride; its oxidation to a dicarboxylic acid could not be effected. The *chloride*, b. p. $170-172^\circ/20$ mm., *ethyl ester* (from the chloride), b. p. $180-183^\circ/15$ mm., *methyl ester*, b. p. $168-170^\circ/15$ mm., *amide*, m. p. 143° , and *anilide*, m. p. $167-168^\circ$, are described. The ester is transformed by an ethereal solution of hydrazine hydrate into a mixture of *bis-2-methyl-1-naphthoylhydrazine*, m. p. 234° , and the normal *hydrazide*, cubes, m. p. 164° . The latter is converted in the usual manner into the

urethane, m. p. 135°, and 1-amino-2-methylnaphthalene. 1-Benzoyl-2-methylnaphthalene, prisms, m. p. 74°, b. p. 240–245°/15 mm., is prepared from 2-methyl-1-naphthoyl chloride and benzene or from benzoyl chloride and 2-methylnaphthalene in the presence of aluminium chloride; it is transformed by aluminium chloride into 6-methylbenzanthrone, bronze-coloured leaflets, m. p. 195°. 1-Bromo-2-methylnaphthalene is converted by the successive action of magnesium in the presence of ether and methyl sulphate into 1:2-dimethylnaphthalene, b. p. 137°/13 mm., d_4^{20} 1.0118 [d_4^{20} 1.011], n_D^{19} 1.60691, n_D^{19} 1.61461, n_D^{19} 1.63613, n_D^{20} 1.6142, (picrate, m. p. 129° after softening at 126°).

β-Naphthylmethyl bromide has b. p. 168–172°/12 mm., Its magnesium compound is converted by acetaldehyde into α,β-di-2-naphthylethane, m. p. 182°. β-Naphthylmethyl bromide and ethyl sodioacetoacetate give ethyl β-naphthylmethylacetoacetate, b. p. 218–220°/13 mm., which is hydrolysed by methyl alcoholic potassium hydroxide solution to β-2-naphthylpropionic acid and α-2-naphthylbutane-γ-one, m. p. 50°, b. p. 190–200°/13 mm. (oxime, needles, m. p. 115–116°; semicarbazone, needles, m. p. 173°). The ketone is reduced to α-2-naphthylbutane, b. p. 125–130°/13 mm., and is hydrolysed to β-naphthylmethylmalonic acid, needles, m. p. 94–95°, from which β-2-naphthylpropionic acid, leaflets, m. p. 134–135°, is prepared. The chloride of the latter acid, m. p. 54°, is converted by aluminium chloride in the presence of light petroleum into 4:5-benzoindan-1-one, colourless needles, m. p. 103°. Ethyl β-naphthylmethylmalonate has b. p. 214–216°/13 mm., and is hydrolysed to β-naphthylmethylmalonic acid, needles, m. p. 94–95°, from which β-2-naphthylpropionic acid, leaflets, m. p. 134–135°, is prepared. The chloride of the latter acid, m. p. 54°, is converted by aluminium chloride in the presence of light petroleum into 4:5-benzoindan-1-one, colourless needles, m. p. 103°. Ethyl β-naphthylmethylmalonate, a colourless liquid, b. p. 225–227°/13 mm., is converted successively into β-naphthylethylmalonic acid, colourless crystals, m. p. 150°, α-2-naphthylmethyl-n-butylric acid, b. p. 225–227°/13 mm. (ethyl ester, b. p. 159–196°/13 mm., amide, needles, m. p. 108°), α-2-naphthylmethyl-n-butylryl chloride, a heavy liquid, b. p. 190–195°/13 mm., and 2-ethyl-4:5-benzoindan-1-one (annexed formula), colourless needles, m. p. 54°, b. p. 195–200°/13 mm., the oxime and semicarbazone of which could not be prepared.

2-Ethyl 4:5-benzoindene has b. p. 157–160°/14 mm., 2:3-Diethyl-4:5-benzoindene, b. p. 205–207°/16 mm., is oxidised by nitric acid to mellophanic acid.

β-Naphthylmethyl bromide and hexamethylenetetramine give an additive compound, colourless leaflets, decomp. 160°, from which β-naphthaldehyde, m. p. 61°, b. p. 155–160°/13 mm., is prepared in 70–80% yield. The aldehyde is converted by nitromethane into β-nitro-α-2-naphthylethylene, yellow needles, m. p. 123°, which is reduced to β-naphthylacetaldoxime, colourless, lustrous needles, m. p. 120°, and β-2-naphthylethylamine, b. p. 160–165°/15 mm., (hydrochloride, m. p. 250° (decomp.); acetyl derivative, m. p. 109–110°).

1-Bromo-β-naphthylmethyl bromide, needles, m. p. 107–108°,

prepared by the bromination of 1-bromo-2-methylnaphthalene at 240—245°, is converted successively into 1-bromo- β -naphthylacetone, needles, m. p. 127·5°, and 1-bromo- β -naphthylacetic acid, needles, m. p. 194° (methyl ester, b. p. 210—215°/18 mm.). It is transformed by hexamethylenetetramine into 1-bromo-2-naphthaldehyde, needles, m. p. 118° (oxime, m. p. 164—166°), which is oxidised to 1-bromo-2-naphthoic acid, needles, m. p. 186°. With ethyl sodiummalonate, the bromide gives ethyl 1-bromo- β -naphthylmethylmalonate, leaflets, m. p. 79—80°, b. p. 250—260°/15 mm., which after hydrolysis and loss of carbon dioxide yields β -1-bromo-2-naphthylpropionic acid, leaflets, m. p. 125° (methyl ester, m. p. 86—87°, chloride, b. p. 210—220°/20 mm., amide, needles, m. p. 164°). 4-Bromo-5:6-benzoindan-1-one, $C_{10}H_5Br \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} CH_2$, has m. p. 152° [oxime, m. p. 222—225° (decomp.)]. Reduction by Clemmensen's method gave a somewhat impure hydrindene, m. p. 92°. H. W.

Isomeric Sulphonimides of Naphthoic Acid, a Contribution to the Theory of Dulcegenic Groups. H. P. KAUFMANN and H. ZOBEL (*Ber.*, 1922, 55, [B], 1499—1508).—A series of substances is described which have a constitution analogous to that of "saccharin" but contain the naphthalene instead of the benzene nucleus. In chemical behaviour they resemble "saccharin" very closely. Unlike the latter, however, they have a pronouncedly bitter taste, which is still more marked in their freely soluble salts with the alkali metals.

β -Naphthylaniline-1-sulphonic acid is diazotised and the product is converted by potassium cuprocyanide solution into 2-cyanonaphthalene-1-sulphonic acid, the potassium salt of which is transformed by phosphorus pentachloride and phosphoryl chloride at 140° into 2-cyanonaphthalene-1-sulphonyl chloride, pale yellow needles, m. p. 92°. The latter is converted by an excess of ammonia dissolved in boiling alcohol into 2-cyanonaphthalene-1- ψ -sulphonamide.

$C_{10}H_6 \begin{smallmatrix} \text{SO}_2 \\ \diagup \quad \diagdown \\ \text{C}(\text{NH}_2) \end{smallmatrix} N$, large, colourless cubes which do not melt below 300°, and is transformed by hot aqueous sodium hydroxide solution into 2-naphthoic-1-sulphonimide ["naphthasaccharin I"] (annexed formula), m. p. 267° (decomp.); the corresponding sodium salt, cubes (+ 2H₂O) and lead salt, anhydrous needles, are described. The sulphonimide condenses with resorcinol in the presence of concentrated sulphuric acid at

150—180° with the production of the corresponding sulpharein.

$C_{23}H_{15}O_6S$.

The preparation of 1-naphthoic-2-sulphonimide ["naphthasaccharin II"] has been described independently by Kalcher (cf. Behrend, A., 1918, i, 413). 1-Cyanonaphthalene-2-sulphonamide, colourless crystals, m. p. 294°, is obtained by the action of the calculated quantity of ammonia on 1-cyanonaphthalene-2-sulphonyl

chloride dissolved in benzene (the corresponding compound obtained by Kalcher is regarded as the ψ -amide). 1-Naphthoic-2-sulphonimide is converted by resorcinol and aluminium chloride into the "saccharein," $C_{23}H_{15}O_5NS$, and by resorcinol and concentrated sulphuric acid into the *sulphurein*, $C_{23}H_{14}O_6S$.

3-Amino-2-naphthoic acid is diazotised and the diazonium compound is transformed into the disulphide, which is reduced by powdered iron in boiling alkaline solution to 3-thiol-2-naphthoic acid. Oxidation with potassium permanganates converts the latter into 3-sulpho-2-naphthoic acid which, with phosphorus pentachloride at 140° , gives the corresponding *dichloride*, pale yellow prisms, m. p. 159° . The latter is transformed by ammonium carbonate into the 2-naphthoic-3-sulphonimide, slender, colourless needles, m. p. 288° ; the *sodium* salt, cubes ($+2H_2O$), and *lead* salt, anhydrous, colourless needles, are described.

1-Cyanonaphthalene-8- ψ -sulphonamide, cubes which do not melt below 300° , is prepared from α -naphthylamine-8-sulphonic acid through the cyanosulphonic acid and the corresponding chloride. It is converted by aqueous sodium hydroxide solution into the 1-naphthoic-8-sulphonimide, colourless needles, m. p. $255-265^\circ$ (decomp.); the corresponding *sodium* salt, cubes ($+2H_2O$), and *lead* salt, colourless, anhydrous needles, are described. H. W.

4-Nitrosalicylic Acid. HEISABURÔ KONDÔ, TOMOICHI NAKAJIMA, and GORÔ MURAKAWA (*J. Pharm. Soc. Japan*, 1922, 355-369).—Ullmann and Uzbachian (A., 1903, i, 626) oxidised 4-nitro-2-acetylaminotoluene with potassium permanganate, and regarded the product as 5-nitro-2-acetylaminobenzoic acid (from its m. p. 221° , etc.). The authors have repeated the work and obtained light yellow needles, m. p. 221° , the decomposition of which by boiling with 15% hydrochloric acid gave 4-nitro-2-aminobenzoic acid, yellowish-red needles, m. p. $263-264^\circ$ (decomp.), giving the ethyl ester, yellow plates, m. p. $97-98^\circ$ (Seidel, 89-91°). The acid was converted into 4-nitrosalicylic acid, small, yellow needles, m. p. $234-235^\circ$ (Ullmann, 226° ; Borsche, 235°), and its ethyl ester, light yellow needles, m. p. $86-87^\circ$. It follows that Ullmann and Uzbachian's acid is 4-nitro-2-acetylaminobenzoic acid. The process is recommended for the preparation of 4-nitrosalicylic acid. The latter was reduced electrolytically to 4-amino-salicylic acid, small, slightly coloured plates, m. p. $149-151^\circ$; hydrochloride, small, yellow leaves, m. p. $222-223^\circ$ (decomp., Seidel, 220°); it gives a purple-red coloration with ferric chloride.

On the other hand, 4- and 5-nitrosalicylic acids and other compounds were prepared from β -nitrophthalimide according to the directions of Seidel and Bittner (*Monatsh.*, 1891, **23**, 435) for comparison with the compounds above described. Correction of m. p. is given in some cases. Ethyl 5-nitro-2-aminobenzoate has m. p. $150-151^\circ$ (Seidel, 146°). 5-Aminosalicylic acid was prepared electrolytically from 5-nitrosalicylic acid. It is unmelted at 260° ; its acid sulphate, white needles, has m. p. $236-237^\circ$ (Beilstein,

234°); the hydrochloride crystallises in hexagonal plates. Its aqueous solution gives an indigo coloration with ferric chloride, thus differentiating it from the 4-isomerides.

K. K.

Polysalicylides. V. PAOLINI and S. SCALBA (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 378—380).—Like the acetyl derivative (*Giorn. Chim. Ind. Appl.*, 1921, **3**, 403), other similar derivatives of salicylic acid, such as benzoyl-, propionyl-, and *n*-butyryl-derivatives and the acetyl compound of Boehringer's diplosal or salicylosalicylic acid (*A.*, 1909, i, 803; 1910, i, 386), undergo decomposition when heated at about their melting points, benzoic, propionic, etc., acid being liberated and a colourless or yellow,

viscous, polymerised salicylide or depside, $\left(\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \right)_n$, formed.

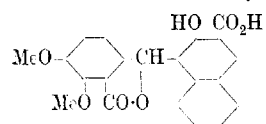
The latter represents a mixture of various polymerides of different complexity, the molecular weight being six to ten times that of salicylide. All these products are converted solely into salicylic acid when hydrolysed by means of alcoholic potassium hydroxide.

T. H. P.

Catalytic Racemisation of Optically Active Acid Amides.

ALEX. MCKENZIE and ISOBEL AGNES SMITH (*T.*, 1922, **121**, 1348—1361).

The Condensation of Methyl β -Naphthol-3-carboxylate with Methyl *n*-Opianate. KARL STOSIUS (*Monatsh.*, 1922, **43**, 43—47).—Opianic acid itself does not condense with methyl 2-hydroxy-3-naphthoate, but its methyl ester condenses slowly in ethereal solution in the presence of hydrogen bromide. The condensation is more sluggish than the



the pseudo- or lactonic form. The condensation product when the methyl ester is used has a lactonic structure (annexed formula).

2-Carboxy-3:4-dimethoxyphenyl-3-carboxy-2-hydroxy- α -naphthyl-carbinol lactone forms pale yellow crystals, m. p. 193.5°. The disodium salt, $\text{C}_{21}\text{H}_{14}\text{O}_7\text{Na}_2$ crystallises in hygroscopic needles, and the dimethyl ester, $\text{C}_{20}\text{H}_{16}\text{O}_7$, forms pale yellow crystals, m. p. 164°.

E. H. R.

The Diphenyleneoxide Series.

FRITZ MAYER and WILHELM KRIEGER (*Ber.*, 1922, **55**, [B], 1659—1666).—The constitution of γ -diphenyleneoxide γ -keto-*n*-butyric and γ -tetrahydrodiphenyleneoxide- γ -keto-*n*-butyric acids has been completely elucidated by the proof that the side chain is attached to the diphenyleneoxide nucleus in position 5.

γ -Diphenyleneoxide- γ -keto-*n*-butyric acid is oxidised by potassium permanganate to diphenyleneoxide-5-carboxylic acid, m. p.

246—247° after softening at 237°. The latter acid is also obtained by the action of bleaching powder on 5-acetyldiphenyleneoxide and from 5-bromodiphenyleneoxide, needles, m. p. 108—109°, b. p. 220°/40 mm., by the successive action of magnesium and carbon dioxide. An acid, m. p. 266°, has been described by Borsche and Bothe as diphenyleneoxide-5-carboxylic acid, but the ultimate proof that the acid, m. p. 246—247°, has this constitution is adduced in the following manner. *p*-Cresol is condensed with *o*-bromonitrobenzene by means of potassium in the presence of naphthalene at 220—230° to 2-nitro-4'-methylidiphenyl ether, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_4\text{Me}$, coarse prisms, m. p. 48—48.5°, b. p. 230—232°/17—18 mm. The latter is reduced by alcoholic ammonium sulphide to 2-amino-4'-methylidiphenyl ether, b. p. 195°/15 mm., which is diazotised and converted into 5-methylidiphenyleneoxide, slender needles, m. p. 45°, b. p. 160°/30 mm.; oxidation of the methyl compound with potassium permanganate gives the acid, m. p. 246—247°.

Ethyl γ -5-diphenyleneoxide- γ -keto-*n*-butyrate, b. p. 260°/2—3 mm., is reduced by amalgamated zinc and hydrochloric acid and the product is re-esterified, thus giving ethyl γ -5-diphenyleneoxide-*n*-butyrate, b. p. 260°/10 mm. Hydrolysis of the latter gives γ -5-diphenyleneoxide-*n*-butyric acid, colourless needles, m. p. 112—113° (chloride, b. p. 170—272°/10—12 mm., amide, colourless leaflets, m. p. 157°). Hydrazine hydrate converts the ester into the corresponding hydrazide, coarse crystals, m. p. 122—123°, which is transformed by sodium nitrite and dilute hydrochloric acid into the acid. The latter is transformed by boiling alcohol into γ -5-diphenyleneoxide-*n*-propylurethane, $\text{C}_{12}\text{H}_9\text{O} \cdot \text{C}(\text{CH}_2)_2\text{NH} \cdot \text{CO}_2\text{Et}$, colourless needles, m. p. 73—74°. Hydrolysis of the urethane with alcoholic potassium hydroxide solution gives γ -5-diphenyleneoxide-*n*-propylamine, b. p. 230—232°/17—18 mm. (hydrochloride, colourless leaflets, m. p. 219—220°, acetyl derivative, colourless needles, m. p. 120°).

γ -5-Diphenyleneoxide- γ -keto-*n*-butyric acid is converted by hydrazine hydrate in boiling alcoholic solution into 3:5-di-phenyleneoxidepyridazin-6-one, $\text{C}_{12}\text{H}_7\text{O} \cdot \text{C} \begin{smallmatrix} \text{N} - \text{NH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CO}$, colourless needles, m. p. 199—200°, which is transformed by bromine in hot glacial acetic acid solution into 3:5-diphenyleneoxidepyridazin-6-one, $\text{C}_{12}\text{H}_7\text{O} \cdot \text{C} \begin{smallmatrix} \text{N} - \text{NH} \\ \diagup \quad \diagdown \\ \text{CH} : \text{CH} \end{smallmatrix} \text{CO}$, colourless needles, m. p. 259—260°. 3:5-Diphenyleneoxide-6-chloropyridazine crystallises in leaflets, m. p. 204—205°.

When dissolved in boiling cyclohexanol, diphenyleneoxide is reduced by sodium to tetrahydrodiphenyleneoxide, b. p. 265—270°.

Ethyl γ -5-tetrahydrodiphenyleneoxide- γ -keto-*n*-butyrate, colourless needles, b. p. 277—278°/23 mm., m. p. 68—69°, is reduced by Clemmensen's method to ethyl γ -5-tetrahydrodiphenyleneoxide-*n*-butyrate, b. p. 253—255°/23 mm., and the latter is hydrolysed to

γ -5-tetrahydrodiphenyleneoxide-n-butyric acid, silver leaflets, m. p. 119–120°. The ester is converted successively into the corresponding *hydrazide*, colourless needles, m. p. 125.5–126.5°, and *urethane*, colourless needles, m. p. 68–69°. Alkaline hydrolysis of the latter leads to the production of *γ -5-tetrahydrodiphenyleneoxide-n-propylamine*, b. p. (about) 220–230°/25 mm. (*hydrochloride*, colourless needles, m. p. 253–254; *acetyl derivative*, leaflets, m. p. 118°).
H. W.

Ring-chain Tautomerism. II. The Effect of the gem-Diethyl Group on the Carbon Tetrahedral Angle. SHANKAR SRIDHAR DESHPANDE and JOCELYN FIELD THORPE (T., 1922, **121**, 1430–1442).

amphoric Acid Derivatives. E. S. FAUST (U.S. Pat., 1406547).—Camphoric acid β -diethylaminoethylimide hydrochloride, colourless, lustrous crystals, m. p. 89–90°, is prepared by heating camphoric acid with *as*-diethylethylenediamine at 180–200°, dissolving in ether, and treating with alcoholic hydrogen chloride. Camphoric acid β -piperidylethylimide hydrobromide has m. p. 193.5°, the β -allylaminoethylimide hydrobromide has m. p. 144°, the β -diethylaminoethylimide hydrobromide has m. p. 157°, the β -dimethylaminoethylimide hydrobromide has m. p. 207°, and the β -aminooethylimide hydrobromide has m. p. 135–140° (decomp.). These compounds have therapeutic uses. CHEMICAL ABSTRACTS.

Dyes Derived from Camphoric Anhydride. ANUKUL CHANDRA SIRCAR and SIKHIBHUSAN DUTT (T., 1922, **121**, 1283–1286).

Optically Active Dyes. I. Camphoreins. BAWA KARTAR SINGH, RAGHUNATH RAI, and RATTAN LAL (T., 1922, **121**, 1421–1430).

Vanillin Glyceride. FRANCIS D. DODGE (*J. Amer. Chem. Soc.*, 1922, **44**, 1405–1407).—A crystalline deposit which had formed in a mixture of alcohol, glycerol, and vanillin was shown to be *vanillin glyceride*, m. p. 160–162°, formed by the condensation of 1 molecule of vanillin with 1 molecule of glycerol. The reaction between these two compounds is much accelerated by the presence of mineral acids, but, on the other hand, the resulting glyceride is readily hydrolysed by acids.
W. G.

Benzopolymethylene Compounds. IV. The Two *ar*-Aldehydes of Tetrahydronaphthalene [Tetralene]. JULIUS VON BRAUN [with K. MOLDAENKE, H. DIRLAM, and H. GRUBER]. (*Ber.*, 1922, **55**, [E], 1700–1709).—Difficulties are encountered in the conversion of tetrahydronaphthalene into the corresponding aldehydes by the action of carbon monoxide, hydrogen chloride, and aluminium chloride, since the greater part of the hydrocarbon undergoes auto-condensation; the small proportion of alde-

hyde produced appears to consist exclusively of the β -derivative. The α -aldehyde is obtained by the following sequence of changes. *ar-x*-Tetrahydronaphthylamine is diazotised and converted into *ar-x*-tetrahydronaphthonitrile, pale yellow crystals, m. p. 48°, b. p. 153°/15 mm. (cf. Bamberger and Bordt, A., 1889, 715), which is converted by fuming hydrochloric acid at 120° into *ar-x*-tetrahydronaphthoic acid, m. p. 150°. Reduction of the nitrile by sodium and alcohol yields tetrahydronaphthalene and *ar-x*-tetrahydronaphthylmethylamine, a colourless liquid, b. p. 149–152°/11 mm.; (the *hydrochloride*, lustrous needles, m. p. 253°, *picrate*, prisms, m. p. 242°, *acetyl* compound, m. p. 125°, *benzoyl* compound, m. p. 144°, *phenylcarbamide*, m. p. 199°, and *phenylthiocarbamide*, m. p. 153°, are described). The amine is converted by sodium nitrite and acetic acid into the corresponding *alcohol*, b. p. 154–155°/12 mm., which is oxidised by potassium dichromate and sulphuric acid to *ar-x*-tetrahydronaphthaldehyde, a colourless, almost odourless liquid, b. p. 131–133°/12 mm. (*semicarbazone*, m. p. 187°). From the preparative point of view, the difficulty involved in this sequence is due to the pooriness of the yields. This has been largely overcome by the subsequent observation that, contrary to the observations of Bamberger and Lodter (A., 1887, 719), α -naphthylmethylamine is directly reducible to *ar-x*-tetrahydronaphthylmethylamine, the process being effected conveniently by sodium and amyl alcohol.

The following derivatives of *ac-x*-tetrahydronaphthylmethylamine are described: *hydrochloride*, m. p. 230°; *picrate*, m. p. 169–170°; *phenylcarbamide*, m. p. 126°; *benzoyl* derivative, m. p. 125°.

ar-β-Tetrahydronaphthonitrile, a colourless liquid, b. p. 151–152°/11 mm., m. p. 20–21°, is reduced by sodium and ethyl alcohol to *ar-β*-tetrahydronaphthylmethylamine, a colourless liquid, b. p. 146–148°/11 mm. (*hydrochloride*, m. p. 248°; *picrate*, m. p. 215°; *benzoyl* derivative, long needles, m. p. 165°, b. p. 260–265°/10 mm., *p-nitrobenzoyl* compound, m. p. 170°; *phenylthiocarbamide*, m. p. 130°). The amine is more conveniently prepared by the reduction of β -naphthylmethylamine by sodium and amyl alcohol; the yield is about 90% of that theoretically possible, but the product appears to be contaminated with very small amounts of the alicyclic derivative. It is converted by sodium nitrite and acetic acid into the corresponding *alcohol*, a pale yellow liquid with a powerful, pleasant odour, b. p. 148–152°/14 mm., which is oxidised to *ar-β*-tetrahydronaphthaldehyde, a colourless liquid with an odour of peppermint, b. p. 138°/14 mm. The corresponding *oxime* has little tendency to crystallise; the *semicarbazone* has m. p. 219°. The aldehyde is smoothly oxidised by potassium permanganate to β -tetrahydronaphthoic acid, m. p. 151°. H. W.

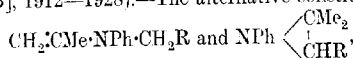
Sulphoacetic Acid as Condensing Agent. IV. *iso*-Acetovanillone. WILHELM SCHNEIDER and EDGAR KRAFT (*Ber.*, 1922, 55, [B], 1892–1899; cf. A., 1921, 4, 680, 859, 879)—*3-Acetoxy-4-methoxyacetophenone* [*acetylisoacetovanillone*], colourless *d d**

leaflets or slender needles, m. p. 66° , is prepared by the regulated action of acetic anhydride (350 c.c.) and concentrated sulphuric acid (50 c.c.) on guaiacol (50 grams) at 80° , and is converted by aqueous alkali hydroxide solutions into 3-hydroxy-4-methoxyacetophenone, m. p. (*monohydrate*) $66-69^{\circ}$, (anhydrous) 91° . The corresponding *oxime*, colourless needles, m. p. 138° , and *semicarbazone*, colourless crystals, m. p. 206° , are described. The constitution of the substance is deduced from its difference from 4-hydroxy-3-methoxyacetophenone [acetovanillone], on the one hand, and from its methylation to 3:4-dimethoxyacetophenone, m. p. $49-50^{\circ}$, and oxidation of the latter to veratric acid, on the other.

Guaiacol is acetylated and anisole is practically unaffected by acetic anhydride containing a trace of concentrated sulphuric acid (2 drops in 40 grams); a perceptible amount of ketone could not be detected in either case.

H. W.

Ketoanils. II. Constitution of the N-Alkylketoanils and Transformation of Aliphatic Ketoanils into Derivatives of Quinoline. E. KNOEVENAGEL and HANS BÄHR (*Ber.*, 1922, 55, [B], 1912-1928).—The alternative constitutions,



have been assigned by Jaeger (A., 1921, i, 785) to the N-alkylketoanils obtained by the fission of ketoanil alkylidides with alkali. A decision in favour of the first formula is reached indirectly, since the alkylidides of compounds with the C:N-linking (methiodides of benzylideneaniline, benzophenoneanil and benzophenone-*p*-tolil) are decomposed when distilled in a vacuum into the same products, which do not contain a three-membered ring, as are obtained by the action of water on them. A more direct confirmation of the non-cyclic structure is based on the observation that methylacetone-*p*-tolil ethiodide is identical with ethylacetone-*p*-tolil methiodide.

Acetoneanil is generally converted by methyl iodide into a glassy methiodide which is transformed by sodium hydroxide into isopropenylmethylaniline [as by-products, a base, $\text{C}_{22}\text{H}_{30}\text{N}_2$, coarse needles, m. p. 147° , and a methiodide (?), m. p. 181° , are isolated]. Acetoneanil is transformed by methyl sulphate into the compound, $\text{C}_{17}\text{H}_{17}\text{O}_4\text{NS}$, silvery leaflets, m. p. 148° , from which methylisopropenylaniline, b. p. $144^{\circ}/14\text{ mm.}$, is obtained in 88.7% yield by means of sodium hydroxide. The base is transformed by nitrous acid into a compound, m. p. $85-91^{\circ}$: it unites with iodine to form methylisopropenylaniline di-iodide, $\text{NPhMe}\cdot\text{CMeI}\cdot\text{CHI}$, m. p. $138-140^{\circ}$.

Benzophenoneanil methiodide, pale yellow needles, m. p. 120° , is converted by dilute sodium hydroxide into benzophenone and aniline.

Benzophenone-p-tolil methiodide, m. p. 198° , is transformed by boiling methyl alcohol into benzophenonedimethylacetal, $\text{CPh}_2(\text{OMe})_2$.

p-toluidine hydriodide, and methyl alcohol. It is hydrolysed by water to benzophenone and *p*-toluidine.

Acetoneanil methiodide decomposes when distilled in a vacuum into hydrogen iodide and methylisopropenylaniline. Benzophenoneanil methiodide and benzophenone-*p*-tolil methiodide are only decomposed slightly under similar conditions.

The *ethiodide* of methylisopropenylaniline, m. p. 244°, is shown to be identical with the methiodide of ethylisopropenylaniline.

Methylisopropenylaniline is converted by hydrogen chloride at 180–200° into methane, methyl chloride, and 2:4-dimethylquinoline, a pale yellow liquid, b. p. 143°/15 mm. (*hydrochloride*, m. p. 210–215° after darkening at 190°; *picrate*, m. p. 194°, *tartrate*, m. p. 158°); the base is also obtained from acetoneanil by an analogous process.

2:4:6-Trimethylquinoline, m. p. 65.5, b. p. 146–148°/13.5 mm., is prepared from acetone-*p*-tolil; the *hydrochloride*, m. p. 268–272° after darkening at 245°, the *tartrate*, m. p. 172°, and the *methiodide*, pale yellow needles, m. p. 245–247°, are described. The base is also obtained from methylisopropenyl-*p*-toluidine.

2:4-Dimethylquinoline can also be prepared from acetoneanil at 280° by the action of aluminium chloride, or from methylisopropenylaniline, phosphorus, and hydriodic acid at 180–200°.

Methylethylketoanil is converted into 2-methyl-4-ethylquinoline, b. p. 150–153°/14 mm. (*methiodide*, m. p. 246°; *tartrate*, needles, m. p. 149°); the volume of ethane liberated is greater than that calculated, and points to non-uniformity in the base. Methyl-ethylquinoline is oxidised by potassium dichromate and sulphuric acid into 2-methylquinoline-4-carboxylic acid, m. p. 244°.

2:6-Dimethyl-4-ethylquinoline, a pale yellow liquid, b. p. 169–171°/20 mm., is obtained from methylethylketone-*p*-tolil; the *tartrate* has m. p. 173°.

H. W.

Ketoanils. III. Fatty-aromatic Ketoanils. E. KNOEVENAGEL and OSKAR GOOS (*Ber.*, 1922, **55**, [B], 1929–1937).—It has been shown by Knoevenagel and Bähr (preceding abstract) that purely aliphatic ketoanils are convertible into quinoline derivatives; this is also true of the mixed fatty-aromatic compounds.

Acetophenoneanil cannot be prepared by the direct action of aniline and acetophenone (whereby 1:3:5-triphenylbenzene is formed), but is produced from the amine and acetophenoneacetal. It is a pale yellow, crystalline substance, m. p. 41°, which is very readily hydrolysed to acetophenone and aniline; the *hydrochloride* has m. p. 190°. When heated at a temperature just below its boiling point, it yields *dypnoneanil*, m. p. 98° ($2\text{CMePh:NPh} \rightleftharpoons \text{NH}_2\text{Ph} + \text{CMePh:CH:CPH:NPh}$, which, when heated further, yields 1:3:5-triphenylbenzene, m. p. 170°. Acetophenoneanil is converted by methyl iodide into *acetophenoneanil methiodide*, colourless rhombohedra, m. p. 209°, and by methyl sulphate into *acetophenoneanil methosulphate*, m. p. 159°; either compound is

*d d 2**

decomposed by dilute aqueous alkali hydroxide or carbonate solution into acetophenone and aniline. Acetophenoneanil hydrochloride is converted by hydrogen chloride at 180–190° into benzene, aniline and 4-phenyl-2-methylquinoline, m: p. 97° (tartrate, m. p. 104°).

Deoxybenzoin is converted by ethyl orthoformate in the presence of alcohol and a trace of hydrogen chloride into *deoxybenzoinacetal*, a colourless, highly refractive liquid, b. p. 172°/14 mm. When heated with aniline, it gives *deoxybenzoinanil*, thin, pale yellow prisms, m. p. 74°, b. p. 215°/13 mm.; it is very readily hydrolysed to deoxybenzoin and aniline. The product thus obtained is an isomeric variety (α -form) of the deoxybenzoinanil, m. p. 89° (β -form), prepared by Busch and Falco (A., 1910, i, 747) from benzanilideimide chloride and magnesium benzyl chloride. The α - is converted into the β -variety when it is heated in a vacuum and subsequently distilled. The former is oxidised to α -benzilanol, m. p. 96°, whereas the latter gives the isomeric β -benzilanol, m. p. 105°. α -Deoxybenzoinanil hydrochloride has m. p. 178–179°. α -Deoxybenzoinanil methosulphate forms lustrous crystals, m. p. 139°. H. W.

The Intermolecular Condensation of Methyl Ethyl Ketone in the Presence of Calcium Carbide. OSCAR BECKER and JOCELYN FIELD THORPE (T., 1922, 121, 1303–1306).

Studies in the Anthracene Series. II. EDWARD DE BARRY BARNETT and JAMES WILFRED COOK (T., 1922, 121, 1376–1391).

Catalytic Reduction of *d*-Camphor. I. SHIGERU KOMATSU and BUNICHI MASUMOTO (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1922, 5, 225–232).—*d*-Camphor was hydrogenated over reduced nickel at 175–185°, and the white, crystalline product fractionally distilled. The main fraction, b. p. 164–165°/757 mm., consisted of a hydrocarbon, C₁₀H₁₈; the last fraction, boiling above 175°, was a mixture of *d*-borneol and unchanged camphor, and the intermediate fractions were mixtures of the above substances. The hydrocarbon was a white, crystalline substance with a pleasant odour, having $[\alpha]_D - 1^\circ 35'$, and was apparently *l*-isocamphane identical with that obtained by Lipp by the catalytic hydrogenation of camphene (A., 1911, i, 731). The same substance was also the main product of the catalytic hydrogenation of both *l*-borneol and *d*-borneol, and it is suggested that the transformation of camphor into *isocamphane* occurs through the formation of borneol, which is

dehydrated to an intermediate product, $\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_2 \\ | \\ \text{CMe}_2 \\ | \\ \text{CH}-\text{C}-\text{CH} \\ | \\ \text{CMe} \end{array}$, which

isomerises to camphene and is then further hydrogenated to *isocamphane*. G. F. M.

Some Derivatives of Fenchone. T. B. MAXWELL (*Ann. Chim.*, 1922, [ix], 17, 332—381).—When reduced by sodium in absolute alcohol, dihydrofencholenamide gives an alcohol and an amine. The alcohol is shown to be dihydrofencholenyl alcohol, identical with that obtained by Semmler from methyl fencholate. With thionyl chloride or phosphorus pentachloride, it does not give the normal chloride, but undergoes molecular transposition, giving *tert*-carvomenthyl chloride, $\text{CHMe}_2\cdot\text{CH}\begin{smallmatrix} \diagup \text{CH}_2\cdot\text{CH}_2 \\ \diagdown \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}\text{CMeCl}$, b. p. $96^\circ/20$ mm., $d_4^{20.7}$ 0.9368, $n_D^{20.5}$ 1.45971, n_D^{25} 1.46202, $n_D^{25.5}$ 1.46811, which was also obtained from carvomenthene by the action of hydrogen chloride. From this chloride by the action of alcoholic ammonia carvomenthene is obtained.

The amine referred to above is shown to be *dihydrofencholenamine*, $\text{CHMe}_2\cdot\text{CH}\begin{smallmatrix} \diagup \text{CH}_2\cdot\text{CH}_2 \\ \diagdown \text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{NH}_2 \end{smallmatrix}$, b. p. $90\text{--}91^\circ/16$ mm., and gives a *hydrochloride*, m. p. $171\text{--}173^\circ$ (decomp.); a *sulphate*, m. p. 190° (decomp.); an *acetate*, m. p. 140° (decomp.); an *acetyl* derivative, b. p. $193^\circ/27$ mm., and a *benzylidene* derivative, b. p. $183\text{--}184.5^\circ/21$ mm. The hydrochloride reacts with nitrous acid to give *tert*-carvomenthol, b. p. $100\text{--}102^\circ/13$ mm., $d_4^{24.6}$ 0.91556, $n_D^{24.6}$ 1.45961, $n_D^{24.6}$ 1.46202, $n_D^{24.6}$ 1.46790, and a hydrocarbon which seems to be identical with carvomenthene.

Dihydrofencholenyl alcohol, when distilled over infusorial earth at $400\text{--}450^\circ$ is dehydrated and gives a *hydrocarbon*, $\text{C}_{10}\text{H}_{18}$, b. p. $60\text{--}61^\circ/16$ mm., $d_4^{24.6}$ 0.81550, $n_D^{24.6}$ 1.45211, $n_D^{24.6}$ 1.45474, $n_D^{24.6}$ 1.46146. Its products of oxidation depend on the agent used. With potassium permanganate in acetone solution it gives *γ*-isopropylpentanone. With hydrogen chloride a certain amount of it is converted into a *chloride*, b. p. $96\text{--}99^\circ/21$ mm., $d_4^{21.9}$ 0.91234, $n_D^{21.9}$ 1.45591, $n_D^{21.9}$ 1.45854, $n_D^{21.9}$ 1.46443, whilst the remainder undergoes isomerisation, giving a *hydrocarbon*, b. p. $67\text{--}70^\circ/16$ mm., $d_4^{21.9}$ 0.81220, $n_D^{20.5}$ 1.45521, $n_D^{20.5}$ 1.45804, $n_D^{20.5}$ 1.46503, which gives a *chloride*, b. p. $100\text{--}101^\circ/23$ mm., $d_4^{23.2}$ 0.92814, $n_D^{23.2}$ 1.45721, $n_D^{23.2}$ 1.45964, $n_D^{23.2}$ 1.46582. To the hydrocarbon is assigned the

constitution $\text{CHMe}_2\cdot\text{CH}\begin{smallmatrix} \diagup \text{CH}_2\cdot\text{CH}_2 \\ \diagdown \text{CH}_2\cdot\text{C}\cdot\text{CHMe} \end{smallmatrix}$

W. G.

The Essential Oil from the Leaves of *Abies Pindrow*, Spach. JOHN LIONEL SIMONSEN (*Indian Forest Rec.*, 1922, 8, 368—372).—The essential oil was obtained in 2.5% yield by the steam distillation of the leaves of *Abies Pindrow*, a silver fir growing in the western Himalayas. It is a colourless oil with a strong odour of turpentine, and has the following constants:— d_4^{20} 0.8558, n_D^{20} 1.4667, $[\alpha]_D^{20}$ —10.38, saponification number 5.3, do. after acetylation 15.44, acid number 0.3. On distillation, 90% passed over below $120^\circ/100$ mm., and on fractionating this under 699 mm. pressure the following fractions were obtained: $154\text{--}158^\circ$,

55.9% consisting of *d*- α -pinene; 158—160°, 11.9%, and 160—164°, 6.8% consisting of a mixture of α - and β -pinene; 164—167°, 4.2%, consisting of *l*- β -pinene; 167—180° 10.3% containing *l*-limonene and possibly dipentene; and above 180° 10.6%, from which and from the fraction boiling above 120°/100 mm., *l*-terpineol, *l*-terpinyl nonoate, and two isomeric sesquiterpene alcohols, $C_{15}H_{24}O$, were isolated. *l*-Terpinyl nonoate boils at 140—145°/50 mm., and the two alcohols were obtained as oils boiling at 155—160°/50 mm., and 180—190°/50 mm., having respectively the constants d_{20}^{25} 0.9076, n_D^{20} 1.4807, $[\alpha]_D^{20} - 7.72$, and d_{20}^{25} 0.9259, n_D^{20} 1.4915, $[\alpha]_D^{20} + 8.1$. No crystalline derivatives could be isolated in either case.

G. F. M.

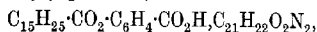
Essential Oil of *Lantana Camara*. K. L. MOUDGILL and P. N. VRIDHACHALAM (*Perf. Essent. Oil Rec.*, 1922, **13**, 173—174).—The essential oil of *Lantana Camara*, a wild shrub growing on waste lands in Southern India, was isolated by steam distillation of the leaves, in a yield of about 0.2%. It is a greenish-yellow, slightly fluorescent oil, having an odour resembling sage. It is soluble in 5 vols. of 97% alcohol, and has the following characters:— d_4^{20} 0.8842, $[\alpha]_D^{20} + 14.7$, n 1.4899, acid value 1.6, saponification value 4.6, acetyl value 23.4, aldehyde content 2.4%. On distillation, three fractions were obtained: (1) 55—75°/12 mm. 12%, (2) 75—125°/12 mm. 8%, (3) 125—130°/12 mm. 74%. The first fraction proved to be *l*- α -phellandrene, the second contained the odoriferous principles which from the oil constants appear to consist mainly of an aldehyde and an alcohol, the third fraction was mainly a bicyclic sesquiterpene closely resembling, if not identical with, caryophyllene, although the solid caryophyllenic alcohol could not be obtained. On redistilling this fraction under ordinary pressure, the original rotation of +16.1° was changed in the distillate to -2.6°. The change does not appear to be a racemisation, as repeated distillation does not modify or remove the lævoration.

G. F. M.

Sudan Essential Oils. A. F. JOSEPH and B. W. WHITEFIELD (*J. Soc. Chem. Ind.*, 1922, **41**, 172t).—"Seid" oil is contained to the extent of about 0.5% in the rhizomes of *Cyperus rotundus*, Linn., a glabrous herb growing freely throughout the Sudan. The oil, which has an aromatic, slightly camphoraceous odour, gave the following constants: d_{20}^{25} 0.9548, $\alpha_D^{25} - 19.9^\circ$, n_D^{25} 1.4967, acid number 1.0, saponification number 6.6, do. after acetylation 165 (corresponding with 45% of alcohol), solubility in 80% alcohol 1 in 4, in 70% alcohol nil.

G. F. M.

Isomeric Amyrols. V. PAOLINI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 374—377; cf. von Soden, A., 1900, i, 401; 1901, i, 159).—By means of the double phthalate formed with strychnine, the author has succeeded in separating amyrol into *d*- and *l*-compounds.

Strychnine d-amyryl phthalate,

forms colourless, acicular crystals, m. p. 201° , $[\alpha]_D + 18^\circ 26'$. d-Amyryl hydrogen phthalate forms a syrup, and d-amyryl a clear, dense, oily liquid of unpleasant odour, b. p. 302° , d^{25}_4 0.982, $[\alpha]_D + 74^\circ 16'$.

Silver l-amyryl phthalate forms crystals, m. p. 145° ; l-amyryl hydrogen phthalate is oily, and l-amyryl is a dense, colourless liquid of unpleasant odour, b. p. 295° , d^{25}_4 0.980, $[\alpha]_D - 1^\circ 59'$.

[No analytical results are given for either amyryl.]

T. H. P.

Mercaptothiazoles as Accelerators in Vulcanisation.

G. BRUNI and E. ROMANI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 86—88; cf. A., 1921, i, 734).—When added to caoutchouc and sulphur in presence of oxide of zinc, lead, magnesium, calcium, mercury, etc., 2-mercapto-5-methylthiazole (cf. Miolati, A., 1893, i, 634), in the proportion of 1—3%, produces ultra-accelerating effects on vulcanisation, which takes place in five minutes at 120° . The zinc, cadmium, lead, mercuric, cobalt, and cuprous salts of this thiazole have been prepared, and the first four of them are found to cause similar accelerating action, which is especially marked with the zinc salt.

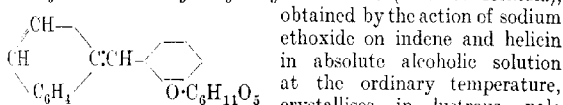
5-Methylthiazole sulphide, $(\text{C}_4\text{H}_4\text{NS})_2\text{S}$, prepared by oxidising 2-mercapto-5-methylthiazole by means of potassium ferrieyanide, forms crystals, m. p. 64° .

T. H. P.

Syntheses of New Glucosides. REMO DE FAZI (*Gazzetta*, 1922,

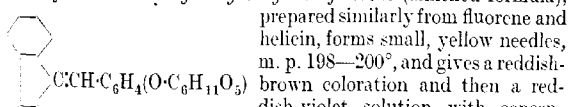
52, i, 429—431; *Atti R. Accad. Lincei*, 1922, [v], **31**, i, 209—212).

—The glucoside of 2-hydroxybenzylideneindene (annexed formula),



obtained by the action of sodium ethoxide on indene and helicin in absolute alcoholic solution at the ordinary temperature, crystallises in lustrous, pale yellow needles, m. p. $205\text{--}206^\circ$, and dissolves in concentrated sulphuric acid to a green solution which becomes cherry-red after a few hours.

The glucoside of 2-hydroxybenzylidenefluorene (annexed formula),



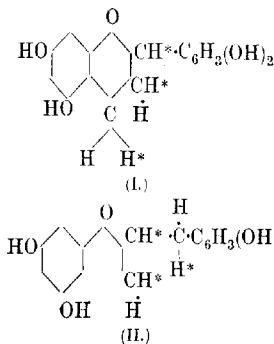
prepared similarly from fluorene and helicin, forms small, yellow needles, m. p. $198\text{--}200^\circ$, and gives a reddish-brown coloration and then a reddish-violet solution with concentrated sulphuric acid; if the latter is added carefully to a solution of the glucoside in absolute alcohol, a reddish-violet ring appears at the surface of contact of the two liquids.

The glucoside of 2-hydroxybenzylideneacenaphthenone (annexed formula), prepared from acenaphthenone and helicin, crystallises in lustrous, pale yellow needles, m. p. 246—248° (decomp.), and dissolves in concentrated sulphuric acid to an orange solution showing green fluorescence. T. H. P.

Benzopyrylium Salts of Distyryl Ketones. JOHANNES SYBRANDT BUCK and ISIDOR MORRIS HEILBRON (T., 1922, **121**, 1198—1212).

• **Catechin.** KARL FREUDENBERG (*Ber.*, 1922, **55**, [B], 1938—1942).—Polemical against Nierenstein (A., 1913, i, 501; T., 1920, **117**, 971, 1151; T., 1921, **119**, 164; T., 1922, **121**, 23).—The author maintains his contention that the tannins are condensation products of catechin-like substances. Attempts to prepare catechin-carboxylic acid according to Nierenstein's directions were unsuccessful, the catechin appearing to be decomposed completely during the action. This is also true of Nierenstein's hydroxycatechin. The catechin-carboxylic acid from *Paullinia* tannin is optically inactive and resolvable: its conversion by loss of carbon dioxide into *d*-catechin (Gambier catechin) is therefore inexplicable. Demethylation of tetramethylcatechin cannot be effected by acetic anhydride and acetyl chloride, and penta-acetylcatechin cannot be hydrolysed to catechin by sulphuric acid as claimed by Nierenstein. The identity of the methylated reduction product of catechin, m. p. 87—88°, with pentamethoxy-*α*-diphenylpropane has been confirmed; Nierenstein's synthesis of acacatechin is therefore difficult to understand since his compounds belong to the *αα*-diphenylpropane group. H. W.

Tannins and Similar Compounds. IX. Stereoisomeric Catechins. II. KARL FREUDENBERG, OTTO BÖHME, and LUDWIG PURRMANN (*Ber.*, 1922, **55**, [B], 1734—1747; cf. A. 1921, i, 576, 799).—It has been shown previously that catechin must be



formulated in accordance with one of the annexed types (I and II), in which one of the hydrogen atoms marked with an asterisk is replaced by the hydroxyl group. If this replacement occurs at the carbon atom united to the oxygen bridge, a single asymmetric carbon atom must be present in catechin, which therefore exists in two active and one racemic form. If, on the other hand, the replacement occurs in a methylene group, two asymmetric carbon atoms are present in catechin,

which therefore exists in two racemic and four active forms.

The latter is shown to be the case, since, under conditions which cause the racemisation of the optically active catechins, *r*-catechin is transformed into *r*-epicatechin, the presence of which is also established in Pegu catechu.

Acacia (Pegu) catechu is exhaustively extracted with ether in a specially designed apparatus which permits the use of large quantities of material and is fully figured and described in the original. The ether is removed from the extract and the residue is crystallised from water whereby mainly *r*- and *l*-catechins are obtained; *l*-epicatechin and *r*-epicatechin are successively obtained from the filtrates, and the fractions are separately purified. *l*-*Epicatechin* crystallises in slender needles and is analysed in the anhydrous condition and as *trihydrate*; the former has decomp. about 228° , $[\alpha]_{\text{D}}^{20} \text{ yellow} -38.4^{\circ}$ in acetone (50%), $[\alpha]_{\text{D}}^{20} \text{ yellow} -41.2^{\circ}$ in alcohol (96%). It gives a *penta-acetate*, colourless needles, m. p. $128-129^{\circ}$, $[\alpha]_{\text{D}}^{20} \text{ yellow} -28.6^{\circ}$ in *s*-tetrachloroethane. *r*-*Epicatechin* crystallises in colourless, thick plates or needles, m. p. 240° (decomp.), and yields a *penta-acetate*, m. p. $169-172^{\circ}$. (The catechin from Chinese rhubarb is shown to be pure *d*-catechin; that from mahogany contains *d*- and *r*-catechin and probably also *d*-epicatechin, but only steamed wood was available for the investigation in which the original catechins had suffered alteration: the catechin from *Paullinia cupana* is similar to that from mahogany.)

d-Catechin penta-acetate readily loses four acetyl groups when treated with potassium acetate and boiling alcohol, giving *d*-catechin *monoacetate*, needles (+2H₂O), m. p. (anhydrous) $120-125^{\circ}$, $[\alpha]_{\text{D}}^{20} \text{ yellow} -19.9^{\circ}$ in acetone (50%). The fifth acetyl group could only be removed under conditions which caused the complete decomposition of the material. Tetramethyl-*d*-catechin has m. p. $146-147^{\circ}$, $[\alpha]_{\text{D}}^{20} -12^{\circ}$ in *s*-tetrachloroethane. Exhaustive methylation of *d*-catechin with methyl sulphate gives pentamethyl-*d*-catechin, m. p. $92-93^{\circ}$, $[\alpha]_{\text{D}}^{20} +8.2^{\circ}$ in *s*-tetrachloroethane. Tetramethyl-*d*-catechin is converted by acetic anhydride and pyridine into tetramethylacetyl-*d*-catechin, m. p. $95-96^{\circ}$, $[\alpha]_{\text{D}}^{20} +6.8^{\circ}$ in *s*-tetrachloroethane.

d-Catechin generally crystallises with 4H₂O; recrystallisation of a considerable quantity of the substance from water gave a small proportion of the anhydrous substance, short, yellow needles, $[\alpha]_{\text{D}}^{20} \text{ yellow} +16.9^{\circ}$ in acetone (50%), $[\alpha] \pm 0^{\circ}$ in alcohol (96%).

The behaviour of *d*-catechin towards gelatin is described; with brucine it gives the additive compound, C₁₅H₁₄O₆.C₂₃H₂₆O₄N₂.
H. W.

Reduction of Flavanone. KARL FREUDENBERG and LEWIG ORTHNER (*Ber.*, 1922, 55, [B], 1748-1751).—In connexion with their work on the catechins, the authors have prepared flavanol

[4-hydroxyflavan], $\text{C}_6\text{H}_4 \begin{array}{l} \text{O} \text{---} \text{CHPh} \\ \text{CH(OH)CH}_2 \end{array}$ since the substance possibly represents the parent of catechin (cf. Freudenberg, Böhme, and Purmann, preceding abstract). It gives a decided, reddish-

violet coloration with concentrated sulphuric acid. This is much more intense than the yellowish-red shade given by tetramethylcatechin, which, however, gradually becomes darker in shade.

Flavanone is reduced by aluminium amalgam in neutral, alcoholic solution to *flavanol*, m. p. 119° corr. (acetate, short, coarse prisms, m. p.

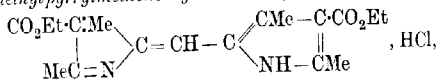
85–86°). The *pinacone*,
$$\begin{array}{c} \text{O} \diagup \text{CHPh} \cdot \text{CH}_2 \quad \text{CH}_2 \cdot \text{CHPh} \diagdown \text{O} \\ \quad \quad \quad \text{C}_6\text{H}_4 - \text{C}(\text{OH}) - \text{C}(\text{OH}) - \text{C}_6\text{H}_4 \end{array}$$
 prisms, m. p. about 250°, is formed as by-product. H. W.

Pyrroles. I. Pyrrolealdehydes. HANS FISCHER and WERNER ZERWECK (*Ber.*, 1922, **55**, [B], 1942–1949).—Under suitable conditions, the Gattermann synthesis of aldehydes by means of hydrocyanic acid and hydrogen chloride can be applied in the pyrrole group.

Ethyl 2:4-dimethylpyrrole-3-carboxylate is converted by hydrogen chloride and cyanide in absolute ethereal solution into the *5-imine hydrochloride*, brown needles, which is decomposed by water into ethyl 2:4-dimethyl-5-aldehydopyrrole-3-carboxylate

$$\text{NH} \begin{array}{c} \text{C}(\text{CHO}) \cdot \text{C} \cdot \text{Me} \\ \diagup \quad \diagdown \\ \text{C} \cdot \text{Me} \quad \text{C} \cdot \text{CO}_2\text{Et} \end{array}$$
 colourless needles, m. p. 165°, the yield

being 95% of that theoretically possible. It gives the typical aldehydic reaction with *p*-dimethylaminobenzaldehyde only when warmed, and does not affect magenta-sulphurous acid solution. The *phenylhydrazone*, pale yellow, lustrous needles, m. p. 163°, *oxime*, colourless crystals, m. p. 168.5° and *semicarbazone*, m. p. 229°, are described. The aldehyde is converted by concentrated nitric acid into ethyl 5-nitro-2:4-dimethylpyrrole-3-carboxylate, m. p. 148°, and by boiling dilute hydrochloric acid into bis-3-carbethoxy-2:4-dimethylpyrrolmethene hydrochloride,



red needles, m. p. 213°. The aldehyde condenses with hippuric acid under the influence of acetic anhydride and sodium acetate giving the *substance*, $\text{C}_{19}\text{H}_{18}\text{O}_4\text{N}_2$, orange-yellow needles, m. p. 175°.

In a similar manner, ethyl 2:5-dimethylpyrrole-3-carboxylate is transformed successively into the *imine hydrochloride* and ethyl 2:5-dimethyl-4-aldehydopyrrole-3-carboxylate, colourless needles, m. p. 151–151.5°. The corresponding *phenylhydrazone*, pale yellow needles, has m. p. 145.5°. The condensation product with hippuric acid, $\text{C}_{19}\text{H}_{18}\text{O}_4\text{N}_2$, crystallises in yellow needles, m. p. 195°.

2:4-Dimethylpyrrole is transformed into the *imine hydrochloride* and 2:4-dimethyl-5-aldehydopyrrole, coarse, colourless needles, m. p. 90°. H. W.

Pyrroles. II. Nitration of Substituted Pyrroles. HANS FISCHER and WERNER ZERWECK (*Ber.*, 1922, **55**, [B], 1949–1955).—The nitration of alkylpyrroles can be effected smoothly with concentrated nitric acid. In the cases of ethyl 5-acetyl-2:4-dimethyl-

pyrrole-3-carboxylate and ethyl 3-acetyl-2:4-dimethylpyrrole-5-carboxylate the nitro-group replaces the acetyl radicle. A similar influence is exerted by the aldehydo-groups. Unexpectedly, the same effect is not produced by the carbethoxy-group since ethyl 2:4-dimethylpyrrole-3:5-dicarboxylate is converted into ethyl 2:4-dinitropyrrole-3:5-dicarboxylate, the methyl groups being replaced by the nitro-residue. Binuclear pyrroles suffer fission at the methylene group uniting the nuclei.

Ethyl 5-acetyl-2:4-dimethylpyrrole-3-carboxylate is converted by nitric acid (*d* 1.4) into ethyl 5-nitro-2:4-dimethylpyrrole-3-carboxylate, colourless needles, m. p. 149.5°; it can also be obtained from ethyl 2:4-dimethyl-5-aldehydopyrrole-3-carboxylate, bis-3-carbethoxy-2:4-dimethylpyrrolmethane or bis-3-carbethoxy-2:4-dimethylpyrrolmethane. 5-Nitro-2:4-dimethylpyrrole-3-carboxylic acid, colourless needles, m. p. 231° (decomp.), is obtained by hydrolysis of the corresponding ethyl ester or by the addition of 5-acetyl-2:4-dimethylpyrrole-3-carboxylic acid to concentrated nitric acid.

Ethyl 3-nitro-2:4-dimethylpyrrole-5-carboxylate, colourless needles, m. p. 204°, is prepared from ethyl 3-acetyl-2:4-dimethylpyrrole-5-carboxylate; 3-nitro-2:4-dimethylpyrrole-5-carboxylic acid darkens at 240° and becomes carbonised at a higher temperature.

Ethyl 2:4-dinitropyrrole-3:5-dicarboxylate crystallises in pale yellow plates (+H₂O), m. p. 136° (decomp.). When heated above its melting point or at 100° in a vacuum, it loses its water of crystallisation and two molecular proportions of nitric oxide, leaving probably a diketo-pyrrole.

H. W.

Relationships between Constitution and Pharmacological Action in the Cases of the Benzoic and Tropic Esters of Hydroxyalkylamines. JULIUS VON BRAUN, OTTO BRAUNSDORF, and KURT RÄTH (*Ber.*, 1922, **55**, [B], 1663--1680).--A series of hydroxyalkylamines of the types $\text{NR}_3 \cdot (\text{CH}_2)_2 \cdot \text{OH}$, $\text{NR}_2 \cdot [\text{CH}_2]_3 \cdot \text{OH}$, $\text{R} \cdot \text{N} \cdot [\text{CH}_2]_2 \cdot \text{OH}$, and $\text{R} \cdot \text{N} \cdot [\text{CH}_2]_3 \cdot \text{OH}$ have been prepared and the hydroxyl hydrogen atom in them has been replaced by the benzoyl (or *p*-aminobenzoyl) or tropoyl groups. It is found that the benzoates of the γ -alkylamines are generally more active physiologically than those of the β -hydroxy-bases, whereas the reverse is the case with the tropates. With regard to the influence of the number of members in the nitrogen ring, it is shown that the six-membered ring is the most active both with respect to the anæsthetising action of the benzoates and the mydriatic and cardiac action of the tropates. The introduction of carbon chains on the nitrogen ring increases the physiological action, but only to a remarkably slight degree. The introduction of an aromatic ring to the monocyclic nitrogen ring diminishes the physiological action, but exact comparison is very difficult in these cases and, in any case, the effect is not important.

The preparation of the substances follows the general lines. The tertiary β -hydroxyalkylamines are obtained by heating the requisite secondary bases with ethylene oxide in chloroform solution to

which a drop of water had been added at 40—60° during several hours by means of ethylene chlorohydrin. Benzoylation is effected by direct warming with benzoyl chloride in chloroform or by agitation with benzoyl chloride and aqueous alkali. The tropoyl group is introduced by heating the alkylamine hydrochlorides with acetyltropoyl chloride, removal of the acetyl group by cold water, and precipitation of the tropic ester with alkali. The benzoates of the γ -series are prepared by warming the requisite secondary base with γ -bromopropyl benzoate.

The following individual compounds are described. β -Dimethylaminoethyl tropate hydrochloride. γ -Dimethylamino-n-propyl tropate hydrochloride. β -Diethylaminoethyl tropate hydrochloride. γ -Diethylamino-n-propyl tropate hydrochloride (the *platinichlorides*, *hydrobromides*, *picrate*, and *methiodides* of the diethyl compounds are oily). γ -Diethylaminopropyl p-nitrobenzoate, a brown liquid which could not be caused to crystallise (*hydrochloride*, m. p. 185—186°; *platinichloride*, m. p. 181°; *picrate*, needles, m. p. 167°; *methiodide*, m. p. 161°). γ -Diethylaminopropyl p-aminobenzoate, a liquid (*hydrochloride*, a liquid; *picrate*, m. p. 132°; *picrate* of the corresponding *acetyl* derivative, m. p. 164—165°). N- β -Hydroxyethylpyrrolidine, a colourless liquid, b. p. 187—189° (*picrate*, m. p. 96°; *methiodide*) and the *hydrochloride* of the corresponding *benzoate*, m. p. 173° after softening at 170°; the *hydrochloride* of the corresponding *tropate* is a transparent liquid. N- β -Hydroxyethylpiperidine *picrate*, yellow prisms, m. p. 100°, and *methiodide*, colourless leaflets, m. p. 238°; *hydrochloride* of the corresponding *benzoate*, m. p. 171—172°. N- β -Tropoxyethylpiperidine *hydrochloride*, a colourless liquid (*hydrochloride* of the corresponding *acetyl* derivative, m. p. 168°). N- γ -Hydroxypropylpiperidine, a colourless, rather viscous liquid, b. p. 228° (*picrate*, m. p. 63—64°; *methiodide*, m. p. 133°). N- γ -Benzoxypropylpiperidine *hydrochloride*, m. p. 185°. N- γ -Tropoxypropylpiperidine *hydrochloride*, a liquid. Hydroxyethylconiine, a colourless liquid, b. p. 117—118°/13 mm. (the *methiodide* and *picrate* are oily; the unusually hygroscopic *hydrochloride* has m. p. about 150°). β -Benzoxyethylconiine *hydrochloride*, a liquid. N- γ -Hydroxypropylconiine *hydrochloride*, a colourless powder, m. p. 162—163°. N- γ -Benzoxypropylconiine *hydrochloride*, m. p. 181—182°. N- β -Hydroxyethylidihydroisoindole, $\text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}\cdot[\text{CH}_2]_2\cdot\text{OH}$, a viscous liquid, b. p. 162—164°/12 mm., (*picrate*, m. p. 125°; *methiodide*, m. p. 130°). N- β -Benzoxyethylidihydroisoindole *hydrochloride*, m. p. 197° (the tropoyl derivative could not be obtained pure). N- γ -Benzoxypropylidihydroisoindole *hydrochloride*, leaflets, m. p. 178—179° (decomp.); the corresponding *base* is a liquid which cannot be distilled without decomposition. The latter when hydrolysed gives a *base*, $\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}$, long prisms, m. p. 63—64°, which contains two atoms of hydrogen and one of oxygen more than the expected γ -hydroxypropylidihydroisoindole; this is not attributable to the presence of firmly combined water of crystallisation, since the difference persists in the salts (*hydrochloride*, liquid; *platinichloride*, long, yellow

needles, m. p. 123°; *picrate*, coarse, lustrous crystals, m. p. 84°); the base, $C_{17}H_{17}O_2N$, gives essentially a *tri-p-nitrobenzoyl* derivative, m. p. 116—118°, which was not obtained in a perfectly homogeneous condition. *N-β-Hydroxyethyltetrahydroisoquinoline*, a colourless, somewhat viscous liquid, b. p. 164—166°/12 mm. (*picrate*, a liquid; *methiodide*, lustrous leaflets, m. p. 147°). *N-β-Benzoxylethyltetrahydroisoquinoline hydrochloride*, m. p. 177—178°. *N-γ-Hydroxypropyltetrahydroisoquinoline*, a transparent, viscous liquid, b. p. 197°/13 mm. (*hydrochloride*, m. p. 151—152°; *picrate*, a liquid; *methiodide*, m. p. 132°). *N-γ-Benzoxylethyltetrahydroisoquinoline hydrochloride*, m. p. 191°; the *hydrochlorides* of the tropic derivatives of β-hydroxyethyl- and γ-hydroxypropyl-tetrahydroisoquinolines are solid but exceedingly hygroscopic. H. W.

Hexamethyleneimine and its Behaviour on Oxidation.

FRIEDRICH SCHMIDT (*Ber.*, 1922, 55, [B], 1584—1591).—Attempts are described to convert hexamethyleneimine into hexamethine-

imine, $\begin{array}{c} \text{CH-CH:CH} \\ \text{CH-CH:CH} \end{array} \rangle \text{NH}$, the latter being required for the comparison

of its properties with those of ψ-aniline (Schmidt, this vol., i, 777). The isolation of the product has not, however, been effected, α-picoline being obtained in its place. A greatly improved method for the preparation of hexamethyleneimine is described and the substance has been more fully investigated.

Ethyl suberate is converted directly by an excess of hydrazine hydrate into suberdihydrazide, m. p. 185—186°, from which (when perfectly pure material is used) the corresponding di-azide, m. p. 26°, is readily produced. The dry azide is transformed by perfectly dry ethyl alcohol into the ethyl urethane (if somewhat moist azide

is employed hexamethylenecarbamide, $[\text{CH}_2]_6 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \rangle \text{CO}$, and the

compound $\text{CO}(\text{NH} \cdot [\text{CH}_2]_6 \cdot \text{NH} \cdot \text{CO}_2\text{Et})_2$ are also produced, the latter of which is gelatinous and greatly complicates filtration). The action of concentrated hydrochloric acid on the urethane gives hexamethylenediamine hydrochloride. Alternatively, the azide is decomposed by ebullition of its solution in anhydrous ether into *hexamethylenedicarbimide*, $\text{C}_6\text{H}_{12}(\text{N}:\text{CO})_2$, a colourless liquid, b. p. 255°, which is readily converted by concentrated hydrochloric acid into carbon dioxide and hexamethylenediamine hydrochloride. The conversion of the diamine into the imine takes place with remarkable readiness, and is conveniently effected by heating the diamine hydrochloride in small portions over a free flame until local carbonisation begins to be observed; the product is rendered alkaline and distilled with steam when the imine is volatilised, whereas the unchanged diamine is not volatile. Hexamethyleneimine is a colourless, mobile liquid with a strong odour of piperidine. It has b. p. 126—127°, d_4^{20} 0.829 [the *picrate* (described previously as a liquid) forms pale yellow crystals, m. p. 85°; the *hydrochloride* is very hygroscopic, the *platinichloride* crystallises in pale yellow platelets, m. p. 191°

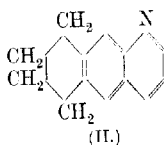
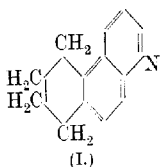
(decomp.), after softening and darkening at about 185° (von Braun has described a monohydrate, m. p. 148°)]. The identity of hexamethyleneimine obtained in this manner with the product described by von Braun is placed beyond doubt by a comparison of the completely methylated products. *Acetylhexamethyleneimine* is a colourless liquid, b. p. 239—241°.

The regulated oxidation of hexamethyleneimine is a problem of considerable difficulty; when dissolved in acetic acid and treated with silver acetate at 180° it gives α -picoline. H. W.

Preparation of *N*-Substituted 3-Dihalogenoxindoles.

ROBERT STOLLÉ (D. R.-P., 341112; from *Chem. Zentr.*, 1922, ii, 35—36; cf. A., 1921, i, 596).—A modification of an earlier patent whereby *N*-trihalogen acetyl derivatives of secondary alkylaryl- or diaryl-amines of the general formula $\text{NRR}'\text{CO}\cdot\text{CX}_3$ ($\text{R}=\text{alkyl}$ or aryl , $\text{R}'=\text{aryl}$, $\text{X}=\text{halogen}$) are heated with aluminium haloids. Ring formation takes place whereby the *N*-dihalogen oxindole derivative is formed with elimination of the corresponding hydrogen haloid, a halogen atom of the trihalogen acetyl group combining with the hydrogen in the ortho-position to the amino-group. 3-Dichloro-1-phenyloxindole is formed by the action of aluminium chloride on trichloroacetyldiphenylamine (from trichloroacetyl chloride and diphenylamine, m. p. 86°) in carbon disulphide solution at the ordinary temperature. By the action of alkalis on it 1-phenylisatin or sodium 1-phenylisatin are obtained. Trichloroacetylmethylanilide (Spiegel and Spiegel, A., 1907, i, 507, 508) gives with aluminium chloride, 3-dichloro-1-methyloxindole. It has m. p. 145° after recrystallisation from methyl alcohol. G. W. R.

Benzopolymethylene Compounds. V. Synthesis of *a*-Anthrapyridine [Naphthazine] from Tetralin [Tetrahydronaphthalene]. JULIUS VON BRAUN and HEINRICH GRUBER (*Ber.*, 1922, 55, [B], 1710—1717).—*or*-5-Tetrahydronaphthylamine is converted by glycerol, concentrated sulphuric acid, and nitrobenzene into a mixture of 5:6- and 6:7-tetramethylenequinolines [7:8:9:10-tetrahydro-5-naphthaquinoline (I) and 6:7:8:9-tetrahydronaphthazine (II)] which can be separated from one another by taking advantage of their widely differing solubilities in hot ethyl alcohol. The former is a colourless crystalline substance.



m. p. 158°, b. p. 183—185°/12 mm., which becomes pink on exposure to air. The hydrochloride, m. p. 236° after darkening at 226°, picrate, m. p. 207°, and methiodide, m. p. 263°, are described. The constitution of the base is established by its dehydrogenation at 700° to β -naphthaquinoline, m. p. 91—92°.

6:7:8:9-Tetrahydronaphthazine is a colourless, crystalline substance, m. p. 71—72°, b. p. 187°/11 mm. It gives a *hydrochloride*, pale yellow needles, m. p. 177°, a *picrate*, m. p. 269.5°, and a *methiodide*, m. p. 187°. The base is dehydrogenated at 720° to naphthazine, colourless crystals, m. p. 114°, b. p. 200—250°/14 mm. The corresponding *hydrochloride*, intensely yellow crystals, m. p. 196—197° after softening at 191°, the *picrate*, m. p. 258° after darkening at 229°, and the *methiodide*, m. p. 225—226°, are described. The base is oxidised by chromic acid in warm glacial acetic acid solution to naphthazinequinone, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_5H_3N$, long, yellow needles.

m. p. 280°. Treatment of naphthazine with tin and concentrated hydrochloric acid effects hydrogenation of the pyridine nucleus, thus giving 1:2:3:4-tetrahydronaphthazine, $C_6H_4 \begin{smallmatrix} \diagup CH \\ \diagdown CH \end{smallmatrix} C_5H_7N$, lustrous leaflets, m. p. 149°. The *hydrochloride* has m. p. 229°. The secondary nature of the base is established by its smooth conversion into a *nitroso-derivative*, golden-yellow leaflets, m. p. 129°.

H. W.

Iodo-derivatives of Pyrrole. ANTONIO PIERONI (*Atti R. Accad. Lincei*, 1922, [v], 31, i, 321—323).—When treated with aqueous potassium hydroxide and iodine, pyrrole-3-carboxylic acid, acetyl- and benzoyl-pyrroles, and indole-2- and indole-3-carboxylic acids undergo iodination, yielding various products in each case. In presence of the required proportion of iodine dissolved in potassium iodide solution and of excess of the alkali, either pyrrole or pyrrole-2-carboxylic acid yields principally tetraiodopyrrole and *hepta-*

iododipyrryl, $\begin{array}{c} \text{Cl}-\text{Cl} \\ \parallel \quad \parallel \\ \text{Cl}-\text{NH} \end{array} \begin{array}{c} \diagup \text{C} \diagdown \\ \diagdown \text{C} \diagup \end{array} \begin{array}{c} \text{Cl}:\text{Cl} \\ \parallel \\ \text{N}-\text{Cl}_2 \end{array}$, which crystallises in silvery

needles, has the normal molecular weight in freezing glacial acetic acid, and decomposes with emission of violet vapour at 166—173°. A blackish-blue powder is also formed in the reaction; this is a product of the condensation and de-iodination of tetraiodopyrrole and when washed with ether gives a residual compound, which contains iodine, exhibits physical properties similar to those of indigotin, and is being investigated further. The above formation of heptaiododipyrryl indicates that, in alkaline solution, tetraiodopyrrole exists in

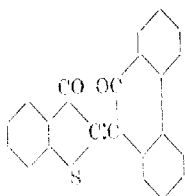
the tautomeric forms, $\begin{array}{c} \text{Cl}:\text{Cl} \\ \parallel \\ \text{NH} \end{array} \begin{array}{c} \diagup \text{C} \diagdown \\ \diagdown \text{C} \diagup \end{array} \begin{array}{c} \text{Cl}:\text{Cl} \\ \parallel \\ \text{N}-\text{Cl}_2 \end{array}$ and $\begin{array}{c} \text{CH}:\text{Cl} \\ \parallel \\ \text{N} \end{array} \begin{array}{c} \diagup \text{C} \diagdown \\ \diagdown \text{C} \diagup \end{array} \begin{array}{c} \text{Cl}:\text{Cl} \\ \parallel \\ \text{N}-\text{Cl}_2 \end{array}$.

Both the tetra- and the hepta-iodo-compounds react in alkaline solution with diazonium salts and with *p*-bromophenylazoxycarbonamide, whilst on reduction in either neutral or alkaline media they yield an oily product which gives a vapour capable of reddening a pine splinter moistened with hydrochloric acid and readily loses part of its iodine to form a black powder insoluble in ordinary solvents.

T. II. P.

Influence of Substituents on the Formation and Stability of Heterocyclic Compounds. 1. Hydantoins. CHRISTOPHER KELK INGOLD, SHINICHI SAKO, and JOCELYN FIELD THORPE (T., 1922, 121, 1177—1198).

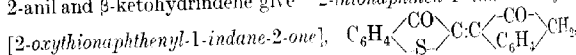
Indigoid Dyes of the Phenanthrene and Indene Series. P. FRIEDLÄNDER, WALTER HERZOG, and G. VON VOSS (Ber., 1922, 55, [B], 1591—1596).—“2-Thionaphthen-



9-phenanthreneindigo” [10-oxy-9-oxythionaphthenyl-6-oxyphenanthrene] (annexed formula), dark violet, almost black crystals, is readily prepared by the addition of a few drops of concentrated hydrochloric acid to a boiling solution of 3-hydroxythionaphthen and phenanthraquinone in acetic acid. It gives dull violet shades from a yellow vat on the textile fibres. The diacetyl compound of the leuco-derivative is described. The dye is remarkable for its stability towards boiling solutions of alkali. For purposes of comparison, the analogously composed 8-oxy-7-oxythionaphthenylacennaphthene (A., 1908, i, 674) has been examined in this respect; it is found to be decomposed with far

greater readiness into thiosalicic acid and *acennaphthenone-7-aldehyde* [annexed formula], m. p. 163° [phenylhydrazone, m. p. 170° (decomp.), methyl ether, colourless needles, phenylhydrazone of the methyl ether, yellow needles, m. p. 172°].

Somewhat unexpectedly, β -ketoindene is found to condense with two molecular proportions of *p*-nitrobenzaldehyde to give the compound $C_{22}H_{14}O_5N_2$, and similarly with *p*-hydroxybenzaldehyde, giving the substance $C_{22}H_{16}O_5$, lustrous, yellow needles, m. p. about 265° (decomp.). It reacts, however, with a single proportion of α -isatin chloride to yield “2-indole-1'-indaneindigo” [2-indoxyl-1-indane-2-one] which is also produced from β -keto-hydrindene and α -isatinanilide in the presence of acetic anhydride. The dye is decomposed with great difficulty by solutions of alkali; it gives very intense, dark bordeaux shades on wool from a pale yellow hyposulphite vat. The composition of the dye is confirmed by the analysis of the similar product, $C_{17}H_9O_2NBr_2$, from β -keto-hydrindene and dibromoisatin chloride. Thionaphthenquinone-2-anil and β -keto-hydrindene give “2-thionaphthen-1'-indaneindigo”



reddish-violet crystals, which dye the textile fibres from a yellow vat in redder shades than the corresponding indole dye. Similarly, thionaphthenquinone-2-anil and $\alpha\gamma$ -indanedione yield “2-thionaphthen-2'-indoneindigo” [2-oxythionaphthenyl-2-indane-1,3-dione] $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown S \end{smallmatrix} C:C \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_4$, slender, reddish-violet needles. H. W.

1:1'-Diphenylindigotin. P. FRIEDLÄNDER and K. KUNZ (*Ber.*, 1922, 55, [B], 1597—1607).—1:1'-Dimethylindigotin (A., 1912, i, 727) differs from the parent substance in its ready solubility in the customary indifferent media, its more basic character, its marked green shade, and its relative instability towards alkalis and acids. In 1:1'-diphenylindigotin, the presence of aromatic residues united to the nitrogen atoms so lessens the stability of the molecule that the substance has no value as a vat dye. The shade is also displaced markedly towards the green, but not to so great an extent as with the methyl derivative.

N-Phenylantranilic acid is converted by hot formaldehyde solution (30%) into the so-called *formalide*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO-O} \\ \diagup \quad \diagdown \\ \text{NPh-CH}_2 \end{smallmatrix}$,

large, pale pink plates, m. p. 89°, which is transformed by a cold, concentrated solution of potassium cyanide into the *nitrile*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CN}$, pale yellow, prismatic crystals, m. p. 133—134°; the latter is converted by concentrated sodium hydroxide solution into *N-diphenylglycine-o-carboxylic acid*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, pale yellow prisms, m. p. 160—163° (evolution of carbon dioxide); the corresponding *methyl* and *ethyl* esters could not be caused to solidify. Similarly, *N-p-chloro-phenylantranilic acid* is transformed successively into the *formalide*, long, almost colourless crystals, m. p. 131—132°, the *nitrile*, prisms, m. p. 146—148°, and *p-chloro-N-diphenylglycine-o-carboxylic acid*, pale yellow crystals, m. p. 184—186°.

Diphenylglycine-o-carboxylic acid loses carbon dioxide when heated with sodium acetate and acetic anhydride, and the product, after being hydrolysed with sodium hydroxide, consists essentially of 1-phenylindoxyl, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C(OH)} \\ \diagup \quad \diagdown \\ \text{NPh} \end{smallmatrix} \text{CH}$, which, however, could not

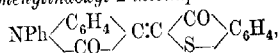
be caused to crystallise. A similar product is obtained from diphenylglycine-o-carboxylic acid and sodium hydroxide at 190—200°. The crystalline *sodium salt* of phenylindoxyl also gives a non-crystalline phenylindoxyl when treated with ammonium chloride. The action of sodium alkoxide on methyl diphenylglycine-o-carboxylate gives *methyl phenylindoxylate*, pale yellow crystals, m. p. 114—115°; the corresponding *ethyl ester* has m. p. 75—76°. Although, however, phenylindoxyl could not be isolated in the homogeneous condition, its presence in the crude products is established by the isolation of 4-chlorophenylindoxyl, long, yellow prisms, m. p. 110—111°, by the similar treatment of the *p-chloro-acid*. In general, the reactivity of phenylindoxyl (and chlorophenylindoxyl) is less than that of the parent substance; thus it could not be condensed with isatin or isatinanilide. With *p*-nitrosodimethylaniline, on the other hand, it gives 1-phenyl-

isatin-2-*p*-dimethylaminoanil, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NPh} \end{smallmatrix} \text{C:N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, prisms, m. p. 173°. The latter is converted by 3-hydroxythionaphthen in

the presence of acetic anhydride into 2'-1-phenylindoxyl-2-thio.

naphthen-3'-one, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{NPh} \diagup \end{array} \text{C}:\text{C} \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{S} \diagup \end{array} \text{C}_6\text{H}_4$, dark red needles.

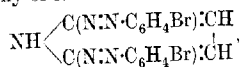
N-Phenylisatin, red needles, m. p. 135—136°, is prepared from phenylindoxyl through the anilide or by direct oxidation of its solution in alcohol and acetic acid with solid ferric chloride; it is also obtained smoothly by the gradual addition of dilute nitric acid to a solution of diphenylindigotin in glacial acetic acid. Boiling sodium hydroxide solution converts phenylisatin into acridine-5-carboxylic acid. Equivalent quantities of 1-phenylisatin and indoxyl react with the formation of *N*-phenylindirubin, needles, m. p. 238°; 3'-1-phenylindoxyl-2-thionaphthen-3-one,



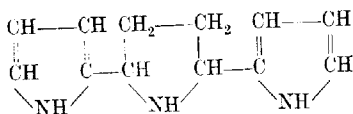
long, red needles, is prepared from phenylisatin and 3-hydroxy-thionaphthen. In a similar manner, 4-chlorophenylindoxyl is converted into 4-chlorophenylisatin, yellow needles, m. p. 197—198°; sodium 4-chlorophenylisatin is also described.

1:1'-Diphenylindigotin, almost black, lustrous plates, is most conveniently prepared by the oxidation of 1-phenylindoxyl by potassium ferricyanide in faintly alkaline solution. The corresponding 1:1'-di-*p*-chlorophenylindigotin is scarcely distinguishable in shade and properties from the chlorine-free dye. H. W.

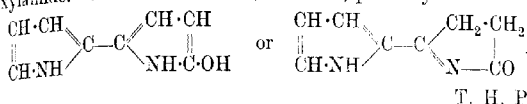
Constitution of certain Polypyrroles. ANTONIO PIERONI and ALDO MOGGI (*Atti R. Accad. Lincei*, 1922, [v], 31, i, 381—385).—Since *p*-bromobenzeneazoxycarboxylamide reacts readily with pyrrole and many of its derivatives to form the compound



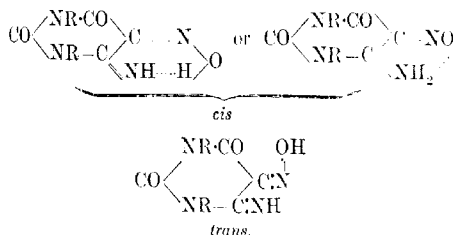
it serves as a reagent for the detection of the pyrrole nucleus. Quantitative investigation of the action of this reagent on tripyrrole (cf. Dennstedt, A., 1887, 598; 1888, 849; 1889, 400; 1894, i, 259) shows that the latter contains in its molecule at least two pyrrole nuclei connected at the 2- or 5-position with a third nucleus. Consequently, the formulae ascribed to tripyrrole by Dennstedt and Voigtländer (A., 1894, i, 259) and by Tschelincev, Tronov, and Voskresenski (A., 1915, i, 1008) cannot be accepted. Further, the ready decomposition of tripyrrole into indole, pyrrole, and ammonia when heated indicates that the third nucleus is a pyrrolidine nucleus, and this indication is confirmed by the observation that oxidation of tripyrrole by means of potassium dichromate and sulphuric acid results in the formation of succinic acid. The conclusion is drawn that tripyrrole has the annexed formula.



As regards hydroxydipyrrole, $C_8H_8ON_2$, it is found that this compound yields pyrrole-2-carboxylic acid when treated with permanganate, forms succinic acid when oxidised with potassium dichromate and sulphuric acid, and gives 2 : 5-di-*p*-bromobenzene-azopyrrole in the proportion corresponding with one pyrrole nucleus in the molecule when treated with *p*-bromobenzeneazoxycarbonylamide. The constitution is, therefore, probably



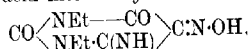
Colour Isomerism and Salt Formation with Iminovioluric Acids. II. I. LIFSCHITZ [and, in part, B. B. HEPNER] (*Ber.*, 1922, 55, [B], 1619—1631).—A further series of iminoviouric acids has been prepared and their chromoisomerism investigated. These metal-free compounds show in every detail the peculiarities which have been observed with the polychromic salts of ordinary violuric acid and related oximino-ketones. Whilst the violuric acids are all colourless, the iminoviouric acids are not merely coloured, but also give an absorption spectrum completely analogous to that of the violurates, whereas the salts with acids absorb similarly to the free violuric acids. Like the violurates, the iminoviouric acids exist in differently coloured modifications which in certain cases can be transformed reversibly into one another. It appears, therefore, that the existence of variochromic phenomena in the case of the violurates and analogous oximino-ketone salts does not depend on the presence of a metallic atom or an external base. It is only necessary that salt formation should occur such as exists in the iminoviouric acids which may be regarded as internal ammonium salts. As is to be expected, the iminoviouric acids behave as typical amphoteric electrolytes. The colour and variochromism of the violurates cannot be explained by their electrolytic character, but only by the arrangement of the subsidiary valencies, thus :



The optical data show that the coloured forms of the acids all belong to the *cis*-series; the colour depends on the presence of the

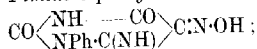
imino-group in the 4-position. They are all internal salts and only bimolar salts to a very slight degree. The trans-structure is characteristic of the unstable colourless forms which are permanent in the acid salts and are directly comparable with the colourless, free violuric acids.

4-Imino-2:6-diketo-1:3-diethylhexahydropyrimidine, colourless crystals, m. p. 127°, is conveniently prepared by heating diethylcarbamide with cyanoacetic acid and acetic anhydride and treatment of the product with sodium hydroxide. It is transformed by nitrous acid into *diethyliminovioluric acid*,



dark red needles which become blue when heated cautiously at 90°. It forms colourless salts with strong acids, of which the hygroscopic *hydrochloride* and *sulphate* and the *hydrobromide* have been examined. With bases it gives yellow, unstable salts which cannot be isolated in the pure condition (*lithium* and *sodium* salts) and very stable red salts (*sodium* and *potassium*).

Cyanoacetylphenylcarbamide, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$, m. p. 198°, is conveniently prepared by the condensation of phenylcarbamide with cyanoacetic acid in the presence of acetic anhydride. It is converted by potassium hydroxide solution (50%) into 4-imino-3-phenylbarbituric acid, leaflets, which does not melt below 230°, which yields 4-imino-3-phenylvioluric acid,



the latter exists in two forms, red needles and bluish-violet crystals, the former of which is the more stable at the atmospheric temperature. A pure blue *variety* was also obtained incidentally during an attempt to isolate the quinine salt. Iminophenylvioluric acid gives colourless salts with acids and coloured, somewhat unstable metallic salts which usually contain alcohol or water of crystallisation (the *sodium*, *potassium*, and *silver* salts are described).

The action of nitrous acid on 4-imino-6-keto-2-methoxytetrahydropyrimidine leads to the formation of *methyliminoisovioluric acid*, $\text{OMe}\cdot\text{C} \left\langle \begin{array}{c} \text{NH}-\text{CO} \\ \text{N}\cdot\text{C}(\text{NH}) \end{array} \right\rangle \text{C:N}\cdot\text{OH}$, pale red to carmine-red crystals

(? + H_2O), which are remarkably stable towards rise of temperature. The red *alkali* salts, pink *barium* salt, bluish-violet *silver* salt and tile-red *silver ammonium* salt are described. The *hydrochloride* was prepared. Methylation of the pyrimidine and subsequent treatment with sodium nitrite and acetic acid gives dimethyl-

iminoisovioluric acid, $\text{OMe}\cdot\text{C} \left\langle \begin{array}{c} \text{NMe}-\text{CO} \\ \text{N}\cdot\text{C}(\text{NH}) \end{array} \right\rangle \text{C:N}\cdot\text{OH}$, which has been

obtained in violet, blue, bluish-green, green, and wine-red modifications. The behaviour of the acid toward bases and mineral acids is precisely similar to that of the iminovioluric acids described previously.

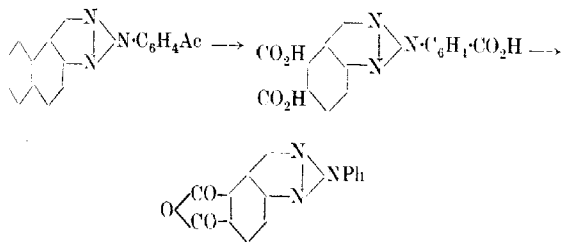
H. W.

Aminoazo-, Hydroxyazo-, and Hydrazo-compounds.

(G. CHARRIER (*Gazette*, 1922, 52, i, 261—277).—The author has shown (A., 1910, i, 287) that *o*-amino-compounds of the benzene and naphthalene series are transformed when heated into *N*-arylbenz- or naphtha-triazoles, *o*-diamines, and primary amines in accordance with the general scheme: $3\text{NH}_2\cdot\text{Ar}''\cdot\text{N}:\text{N}\cdot\text{Ar}' \rightarrow 2\text{Ar}''\cdot\text{N}_3\cdot\text{Ar}' + \text{Ar}'(\text{NH}_2)_2 + \text{Ar}\cdot\text{NH}_2$. It is now shown that a similar reaction is shown by *o*-aminoazobenzene, which decomposes at above 300° into 2-phenylbenztriazole, *o*-phenylenediamine, and aniline. The structure of *o*-aminoazobenzene, established by Witt (A., 1912, i, 321) by means of its reduction, is confirmed by its conversion into *o*-hydroxyazobenzene.

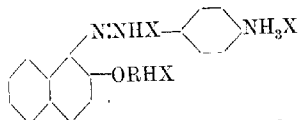
The synthesis of 2-*p*-aminophenyl- $\alpha\beta$ -naphthatriazole has been effected in two ways: (1) *p*-nitrobenzenesazo- β -naphthylamine (Meldola and Hughes, T., 1891, 59, 372) is either heated or oxidised by means of chromic acid in acetic acid solution, the corresponding nitrotriazole thus obtained being then reduced; (2) β -naphthylamine is treated with *p*-acetylaminophenyldiazonium chloride, the resulting *o*-aminoazo-compound being then oxidised and deacetylated. This aminoarylnaphthatriazole is the first such compound which has been prepared.

p-Acetylbenzenesazo- β -naphthylamine yields 2-*p*-acetylphenyl- $\alpha\beta$ -naphthatriazole when oxidised by means of chromic acid in acetic acid solution, but when heated it undergoes a more complex reaction, which appears to consist first of formation of the keto-triazole according to the scheme, $3\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\text{Ac} = 2\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{N}\cdot\text{C}_6\text{H}_4\text{Ac} + \text{C}_{10}\text{H}_6(\text{NH}_2)_2 + \text{NH}_2\cdot\text{C}_6\text{H}_4\text{Ac}$, followed by condensation of the ketotriazole with the naphthylenediamine to a compound, m. p. 288° , now being investigated. Oxidation of 2-*p*-acetylphenyl- $\alpha\beta$ -naphthatriazole by means of alkaline permanganate solution appears to yield the tricarboxylic acid, *vic.* 2-*p*-carboxyphenylbenztriazole-4 : 5-dicarboxylic acid, which loses water and carbon dioxide when fused, with formation of 2-phenyl-*p*-benztriazole-4 : 5-dicarboxylic anhydride:

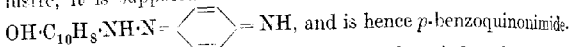


1-*p*-Aminobenzenesazo- β -naphthol, prepared by treating β -naphthol

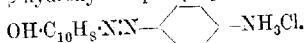
in alkaline solution with *p*-acetylaminobenzenediazonium chloride and hydrolysing the resulting acetyl derivative, is a stable compound and, when subjected to the action of alkyl sulphates in presence of excess of alkali, undergoes etherification at the naphtholic hydroxyl. The ethers thus formed are obtained as dense, impure oils, and react with acids giving crystalline salts which contain three univalent acid residues (X) and have probably the general formula,



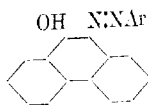
By diazotisation *p*-aminobenzeneazo- β -naphthol may be converted into the corresponding *p*-hydroxyazo-compound. Since *p*-aminobenzeneazo- β -naphthol hydrochloride is pale red whereas the free base is deep brownish-red with a cantharides-green, metallic lustre, it is supposed that the base has the quinonoid structure



β -hydroxy- α -naphthylhydrazone, and that the salt has the formula



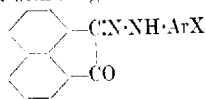
The following compounds have also been prepared: 9-*o*-, 9-*m*-, and 9-*p*-nitrobenzeneazo-10-phenanthrols, 9-*p*-bromobenzeneazo-10-phenanthrol, and 9-*p*-acetylbenzeneazo-10-phenanthrol. These compounds may be obtained either by the action



of diazonium salts on 10-phenanthrol or by the action of the arylhydrazine hydrochloride on phenanthraquinone, the latter reaction giving first the arylhydrazone, which rapidly undergoes transformation into the hydroxyazo-compound.

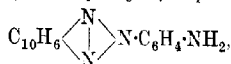
They crystallise well, are highly stable, dissolve in concentrated sulphuric acid giving reddish-violet solutions, and have the annexed general formula.

Acenaphthenequinone behaves like dibromoanthrone towards arylhydrazines, giving the arylhydrazones, whereas phenanthraquinone gives hydroxyazo-compounds under similar conditions. Acenaphthenequinone *o*-, *m*-, and *p*-nitrophenylhydrazones and *p*-acetylphenylhydrazone, prepared by treating the quinone in acetic acid solution with the hydrochlorides of the respective hydrazines, correspond with the general formula,



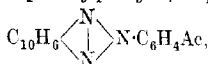
[With C. SALA].—The action of nitrous acid on *o*-aminobenzene yields *o*-hydroxyazobenzene.

[With S. VIOLA.]—2-*p*-Aminophenyl- $\alpha\beta$ -naphthatriazole,



forms slender, straw-yellow crystals, m. p. 198--199°, and is rapidly turned brown by the action of air and light. It dissolves sparingly in dilute mineral acids, forming the corresponding salts, which are readily hydrolysed by water; the sulphate crystallises in minute, lustrous scales. *p*-Acetylaminobenzeneazo- β -naphthylamine forms slender, red needles with brownish-green, metallic reflexion, m. p. 203°.

[With G. CRIPPA.]—2-*p*-Acetylphenyl- $\alpha\beta$ -naphthatriazole,



crystallises in slender, straw-white needles, m. p. 185°, is a highly stable compound, and dissolves in concentrated sulphuric acid, giving an intense yellow solution. Its *p*-bromophenylhydrazone, $\text{C}_{24}\text{H}_{18}\text{N}_5\text{Br}$, forms, thin, lustrous, yellow leaflets, m. p. 215°, and is phototropic; its phenylhydrazone, pale yellow leaflets, m. p. 181°, darkening in the light; its oxime, microscopic, yellowish-white crystals, m. p. 253°, and the *o*-nitrophenylhydrazone, reddish-yellow leaflets, m. p. 180°. These arylhydrazones dissolve in concentrated sulphuric acid, giving yellow colorations similar to that with the ketotriazole itself, but the oxime yields an almost colourless solution.

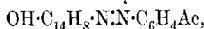
vic. 2-*p*-Carboxyphenylbenzotriazole-4 : 5-dicarboxylic acid, $\text{C}_{15}\text{H}_8\text{O}_6\text{N}_3$, forms minute, white crystals, m. p. 291--292° (decomp.). decomposes carbonates, and is strongly acid to litmus in aqueous or aqueous-alcoholic solutions; the anhydride has m. p. 225--230° (impure).

p-Acetylbenzeneazo- β -naphthylamine, obtained by the action of *p*-acetylbenzenediazonium chloride on β -naphthylamine in alcoholic solution, crystallises in long, flat, intensely red needles, with brilliant metallic green lustre, m. p. 170°, and dissolves in concentrated sulphuric acid with a deep wine-red coloration. It yields a *p*-bromophenylhydrazone, $\text{C}_{24}\text{H}_{20}\text{N}_5\text{Br}$, bright red leaflets, m. p. 217°; a phenylhydrazone, thin, garnet-red leaflets, m. p. 187°, giving a violet-blue solution in concentrated sulphuric acid, and an oxime, which crystallises in dense, garnet-red prisms, m. p. 206°, and dissolves in concentrated sulphuric acid, giving a solution red by transmitted and indigo-blue by reflected light.

[With C. CORTASSA.]—*p*-Acetylaminobenzeneazo- β -naphthol, $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$, forms slender, bright red needles, m. p. 259--260°, and gives a red solution in concentrated sulphuric acid, *p*-Aminobenzeneazo- β -naphthol, $\text{C}_{16}\text{H}_{13}\text{ON}_3$, crystallises in reddish-brown needles with metallic or golden lustre, m. p. 159--160°, and forms a hydrochloride, $\text{C}_{16}\text{H}_{13}\text{ON}_3 \cdot \text{HCl}$, crystallising in slender, pale red needles with golden lustre and yielding a bright red powder.

The *methyl ether*, $C_{17}H_{15}ON_3$, obtained by the action of methyl sulphate in large excess on the base in presence of 30% sodium hydroxide solution, forms a dense, reddish-brown oil. The *ethyl ether* forms a dense oil, and gives a *nitrate*, $C_{16}H_{17}ON_3 \cdot 3HNO_3$, crystallising in slender, metallic green needles, m. p. 95–96° (decomp.), and a *hydrochloride*, $C_{18}H_{17}ON_3 \cdot 3HCl$, forming slender crystals with metallic green lustre, both salts being readily decomposed by water; the ethyl ether is easily hydrolysed to *p*-amino-benzeneazo- β -naphthol when boiled with a dilute acid.

[With L. DEMICHELIS.] — 9-*p*-Bromobenzeneazo-10-phenanthrol, $OH \cdot C_{14}H_8 \cdot N : N \cdot C_6H_4Br$, crystallises in small, bright red needles, m. p. 188°; 9-*p*-acetylbenzeneazo-10-phenanthrol,



in slender, brick-red needles, m. p. 219°; 9-*o*-nitrobenzeneazo-10-phenanthrol, $C_{20}H_{13}O_3N_3$, in slender, bright red, acicular crystals with golden lustre, m. p. 185°, giving a violet-red solution in concentrated sulphuric acid; the 9-*m*-isomeride in orange-red needles, m. p. 196–197° (decomp.), and the 9-*p*-isomeride in garnet-red, flat needles, m. p. 185°. The compound described by Hyde (A., 1899, i, 688) as phenanthraquinone *p*-nitrophenylhydrazone has m. p. 245°.

[With M. SPEIPANL.] — Acenaphthenequinone *o*-nitrophenylhydrazone, $\left\{ \begin{array}{l} C_{10}H_6 \\ CO \end{array} \right\} : N \cdot NH \cdot C_6H_4NO_2$, crystallises in slender, lustrous,

orange-red needles, m. p. 249°; the *m*-nitrophenylhydrazone forms golden-yellow needles, m. p. 229–230°, the *p*-nitrophenylhydrazone, slender orange-red needles, m. p. 247°, and the *p*-acetylphenylhydrazone, $C_{20}H_{11}O_2N_2$, heavy, reddish-brown prisms, m. p. 244–245°. All these hydrazones dissolve in concentrated sulphuric acid, giving ruby-red colorations.

T. H. P.

The Occurrence of Free Radicles in Chemical Reactions. The Radicles of the Basic Triphenylmethane Dyes. HEINRICH WIELAND, EGON POPPER, and HERMANN SEEFRIED (*Ber.*, 1922, 55, [B], 1816–1834).—An experimental examination of the probability of the occurrence of free radicles during the course of simple chemical changes has been commenced. For example, in the case of phenylazotriphenylmethane it is possible that decomposition occurs with the formation of nitrogen, triphenylmethyl and phenyl (and that the two latter combine to a slight extent as shown by Gomberg with the formation of tetraphenylmethane). On the other hand, it is conceivable that the free valencies remain in mutual attraction and that combination between them occurs before the components separate as free radicles.

The decomposition of phenylazotriphenylmethane has been studied in light petroleum, b. p. 90–120°, xylene, and ethyl benzoate. In all cases it is found that nitrogen is evolved completely at a temperature considerably below the melting point of the compound

(80°). In all fissions, triphenylmethyl is produced; it is identified by its spectrum, and its appearance in hot and cold solution, and is isolated after treatment with air or oxygen in the form of its peroxide. The varying yields attained their maximum in one experiment, in which 35% of the theoretically possible quantity was produced. The observations indicate beyond all doubt that the azo-compound decomposes with the formation of radicles. The fate of the phenyl radicle is less easily ascertained. Experimental confirmation of the obvious hypothesis that it becomes polymerised to diphenyl could not be obtained. It is shown, however, that phenyl is found as benzene (*p*-chlorophenyl as chlorobenzene and *p*-nitrophenyl as nitrobenzene) at the conclusion of the reaction. The partner in the change which is poorer in hydrogen has not yet been identified.

The observations have been extended to azo-compounds containing the phenyl group and a group similar to those contained in the basic triphenylmethane dyes, for example, phenylazobis-*p*-dimethylaminotriphenylmethane, $\text{NPh} \cdot \text{NPh}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$. These substances with equal definiteness decomposed, with the formation of free radicles. It is very remarkable that bis-*p*-dimethylamino- and tri-*p*-dimethylamino-triphenylmethyl are scarcely more intensely coloured than triphenylmethyl itself. The radicles and their peroxides are very unstable. The observations are considered to bring important confirmation of the quinonoid structure of the triphenylmethane dyes.

The following compounds do not appear to have been described previously. *p*-Chlorophenylazotri-*p*-tolylmethane, from tri-*p*-tolyl chloromethane and *p*-chlorophenylhydrazine and subsequent oxidation of the product with bromine water, intensely yellow crystals, decomp. 116°. Phenylhydrazotri-*p*-anisylmethane, colourless prisms, m. p. 154° (decomp.). Phenylazotri-*p*-anisylmethane, from the preceding compound and silver oxide, large yellow prisms, m. p. 106° (decomp.). Phenylhydrazobis-*p*-dimethylaminotriphenylmethane, colourless crystals, m. p. 170° (decomp.). Phenylazobis-*p*-dimethylaminotriphenylmethane, a golden-yellow, crystalline powder, m. p. 120° (decomp.). Bis-*p*-dimethylaminotriphenylmethyl peroxide, a colourless, amorphous solid which rapidly darkens and resinifies. *p*-Chlorophenylhydrazobis-*p*'-dimethylaminotriphenylmethane, colourless crystals, m. p. 124.8°. *p*-Chlorophenylazobis-*p*'-dimethylaminotriphenylmethane, slender, golden-yellow needles, decomp. 116°. Phenylhydrazotri-*p*-dimethylaminophenylmethane, needles, m. p. 172° (decomp.). Phenylazotri-*p*-dimethylaminophenylmethane, m. p. 150° (decomp.). *p*-Chlorophenylhydrazotri-*p*'-dimethylaminophenylmethane, plates, m. p. 178° (decomp.). *p*-Chlorophenylazotri-*p*'-dimethylaminophenylmethane, golden-yellow prisms, decomp. 142°. Phenylhydrazotri-*p*-aminophenylmethane, colourless needles, m. p. 200° (decomp.). Phenylazotri-*p*-aminophenylmethane, small, golden-yellow needles, m. p. 195° (decomp.). *p*-Chlorophenylhydrazotri-*p*'-aminophenylmethane,

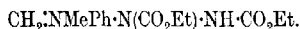
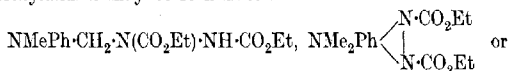
colourless leaflets, m. p. 204° (decomp.), which is dehydrogenated with difficulty.

H. W.

Diazo-compounds. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1922, [v], 31, i, 283—293).—The author criticises a number of statements made by Hantzsch and Reddelien ("Die Diazoverbindungen," 1921), especially from the point of view of priority, and states that no mention is made of some of his own work.

T. H. P.

The Azo-ester Reaction of Amines and Enols. OTTO DIELS (*Ber.*, 1922, 55, [B], 1524—1528; cf. Diels and Fritzsche, A., 1911, i, 957; Diels and Paquin, A., 1913, i, 839; Diels and Fischer, A., 1914, i, 989; Diels, A., 1921, i, 280).—Azodicarboxylic ester unites with amines to give additive compounds of three distinct types: (1) compounds in which the azo-ester is united to the aromatic nucleus [naphthylamine type], (2) compounds which are stable in themselves but are only attacked by reagents after fission into amine and azo-ester [aniline type], and (3) compounds which are decomposed by acids with production of formaldehyde, hydrazo-ester and secondary base [dimethylaniline type]. The initial product in every case appears to have the constitution $\text{NHR}\cdot\text{N}(\text{CO}_2\text{Et})\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, and reaction stops at this point with the aniline type. With the naphthylamine type, on the other hand, a sufficiently activated double bond or hydrogen atom appears to be present to enable the azo-ester to unite with the nucleus, thus giving, for example, $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{N}(\text{CO}_2\text{Et})\cdot\text{NH}\cdot\text{CO}_2\text{Et}$. The constitution of the additive products derived from tertiary amines cannot yet be decided definitely; thus the compound with dimethylaniline may be formulated



The hypothesis that the azo-ester action depends on the additive power of a sufficiently activated double bond or on the mobility of a hydrogen atom is greatly strengthened by the observation that enols, apparently without exception, combine with azo-esters. Thus methyl azodicarboxylate and ethyl acetoacetate yield the compound $\text{C}(\text{OMe})\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{N}(\text{CO}_2\text{Me})\cdot\text{NH}\cdot\text{CO}_2\text{Me}$, m. p. 113°, and ethyl azodicarboxylate reacts readily with acetylacetone in the presence of potassium acetate, giving $\gamma\text{-NN}'\text{-dicarbethoxyhydrazinoacetylacetone}$, $\text{CH}(\text{COMe})_2\cdot\text{N}(\text{CO}_2\text{Et})\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, colourless, lustrous prisms, m. p. 123°.

The previous hypothesis that azo-esters react only with aromatic amines is now abandoned owing to the observation that ethyl β -aminocrotonate combines with methyl azodicarboxylate to give the compound $\text{NH}_2\cdot\text{CMe}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{N}(\text{CO}_2\text{Me})\cdot\text{NH}\cdot\text{CO}_2\text{Me}$, m. p. 140°.

The communication is of a preliminary nature, the full experimental details being promised for a subsequent paper. H. W.

Decomposition of Benzyl Azide in Indifferent Media and in Malonic Ester. THEODOR CURTIUS and GUSTAV EHRRHART (*Ber.*, 1922, **55**, [B], 1559—1571).—Benzyl azide is decomposed when heated in xylene, but the stable residue, $\text{CH}_2\text{Ph}\cdot\text{N}\cdot$, unlike that derived from benzenesulphonazide, is unable to combine with the hydrocarbon, which itself takes no further part in the chemical changes. Addition, however, does occur with substances such as ethyl malonate and ethyl methylmalonate, with production of ethyl benzylaminomalonate, $\text{CH}(\text{CO}_2\text{Et})_2\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, and ethyl benzylmethylaminomalonate.

A modified process for the preparation of benzyl azide, b. p. $82.5^\circ/16.5$ mm., from benzyl chloride and sodium azide, is described in detail, the yield being 90% of that theoretically possible.

Benzyl azide decomposes very slowly in the presence of boiling xylene, and the action is therefore effected under pressure in a specially designed glass autoclave at 170 — 180° . *Dibenzylbenzoamidine*, $\text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{CPh}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, a microcrystalline, feebly anisotropic substance, m. p. 106° , separates from the solvent [the corresponding *sulphate*, $\text{C}_{21}\text{H}_{20}\text{N}_2\cdot\text{H}_2\text{SO}_4$, coarse, colourless plates, m. p. 233° , *picrate*, prisms, m. p. 254° (decomp.), and *acetate*, coarse platelets, m. p. 299° (decomp.), are described]; the constitution of the substance is deduced from its hydrolysis by aqueous barium hydroxide solution at 120° to benzylamine and benzoic acid. The filtrate from the dibenzylbenzoamidine is distilled with steam, whereby tribenzylamine, m. p. 91° , is volatilised; the residue contains tetraphenylpyrazine, $\text{N}\langle\text{CPh}\cdot\text{CPh}\rangle\text{N}$, and diphenylbenzylpyrroldiazole,

$\text{CH}_2\text{Ph}\cdot\text{N}\cdot\langle\text{CPh}\cdot\text{N}\rangle$, m. p. 229° . In a second experiment, in which

the excess of xylene was immediately distilled and the total residue treated with steam and dissolved in ether, it was found possible to isolate benzylbenzylideneamine, $\text{CHPh}\cdot\text{N}\cdot\text{CH}_2\text{Ph}$, b. p. $230^\circ/20$ mm., whilst, on another occasion, the mother-liquors from the tetraphenylpyrazine and diphenylbenzylpyrroldiazole yielded a very small quantity of a substance, small needles, m. p. 186° , which gave benzaldehyde when gently warmed with acids and appeared to be a *polymeric benzylbenzylideneamine*, although the quantity of substance available was insufficient for an extended investigation. In the presence of boiling cymene, the decomposition of benzyl azide follows much the same course, but tetraphenylpyrazine is produced in rather larger quantity. In the presence of dimethylaniline at 170 — 180° , tetraphenylpyrazine is not produced, but more diphenylbenzylpyrroldiazole is obtained; the formation of dibenzylbenzamidine is not observed. The hypothesis is advanced that the initial decomposition of benzyl azide results in the production of the radicals $\text{CH}_2\text{Ph}\cdot\text{N}\cdot$ and (by loss of hydrazoic acid) $\text{Ph}\cdot\text{CH}\cdot$. Immediate union of these leads to the formation of benzylbenzylideneamine; addition of the residue, $\text{CH}_2\text{Ph}\cdot\text{N}\cdot$, to the latter results in the production of dibenzylbenzamidine.

The occurrence of diphenylbenzylpyrroldiazole seems to be coupled with that of tribenzylamine and can be explained in the following manner. The radicle $\text{CH}_2\text{Ph}\cdot\text{N}\cdot$ passes into its imino-form, $\text{CHPh}\cdot\text{NH}$, which loses two atoms of hydrogen, these being utilised in the reduction of two PhCH residues. A new radicle, $\text{C}\cdot\text{Ph}\cdot\text{N}\cdot$, thus arises from which the unsaturated residue, $-\text{CPh}\cdot\text{N}\cdot\text{N}\cdot\text{CPh}\cdot$ is formed; combination of the latter with the radicle $\text{CH}_2\text{Ph}\cdot\text{N}\cdot$ yields diphenylbenzylpyrroldiazole. Tribenzylamine is formed in accordance with the scheme: $2\cdot\text{CH}_2\text{Ph} + \text{CH}_2\text{Ph}\cdot\text{N}\cdot \rightarrow \text{N}(\text{CH}_2\text{Ph})_3$.

The decomposition of benzyl azide in the presence of ethyl malonate at 170° differs from its reactions just described in that hydrazoic acid does not appear to be eliminated, and that complications caused by the occurrence of the radicle $\cdot\text{CHPh}$ are thus completely excluded. Reaction proceeds along simpler lines and results in the production of ethyl benzylaminomalonate, which, however, could not be isolated in the homogeneous condition. The hydrolysis of the crude ester by aqueous potassium hydroxide gives benzylaminomalonic acid, m. p. 115° (decomp.), whereas it yields benzylaminoacetic acid hydrochloride when treated with hydrochloric acid at 110° . Similarly, benzyl azide and ethyl methylmalonate react to form ethyl benzylaminomethylmalonate, from which impure benzylaminomethylmalonic acid is derived (it evolves carbon dioxide at the atmospheric temperature). The crude ester is transformed by concentrated hydrochloric acid at 120° into α -benzylaminopropionic acid hydrochloride, pale yellow, coarse, rectangular, anisotropic plates.

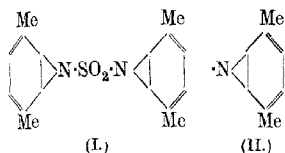
H. W.

The Action of Sulphuryl Azide on *p*-Xylene. THEODOR CURTIUS and FRIEDRICH SCHMIDT (*Ber.*, 1922, **55**, [B], 1571—1581).—Sulphuryl azide is prepared in a not quite homogeneous condition by the action of sulphuryl chloride on finely divided, slightly moist sodium azide. In contrast to the azides of organic sulphonic acids, it is violently explosive, frequently without apparent cause. Its decomposition in *p*-xylene solution (3%) begins at about 70° , and is completed by very gradually raising the temperature of the solution during about a week and continuing the process until further evolution of gas does not occur from the briskly boiling mixture. The unusual course of the change is indicated by the evolution of large quantities of sulphur dioxide. After removal of the *p*-xylene, the residue is made alkaline and distilled with superheated steam. The mixture of bases is separated and distilled, when a solid base (*C*, see below) separates from the distillate. This is removed, and two further bases (*A* and *B*) are isolated in the form of the picrates from the filtrate, which also yields a neutral substance, *D*. The work is rendered unusually difficult by the danger of the operations, the minimal yields of well-defined products and their close resemblance to one another. The actual substances isolated are the following. Base *A*, ψ -xylidine, $\text{C}_8\text{H}_{11}\text{N}$, a liquid with an odour of pyridine, which gives a very hygroscopic hydro-

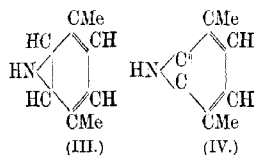
chloride, a *picrate*, m. p. 152°, moderately soluble in alcohol or water, two *platinichlorides*, pale yellow crystals, m. p. 148°, and dark yellow crystals, m. p. 181°, respectively; a liquid base *B*, C_8H_9N , with pyridine-like odour, yields a non-hygroscopic *hydrochloride*, m. p. 212–213°, a *picrate*, m. p. 239°, which is sparingly soluble in alcohol or water, and a *platinichloride*, plates, m. p. 260°; a solid, odourless, crystalline base *C*, C_8H_9N , m. p. 112°, which gives a non-hygroscopic hydrochloride, m. p. 218°, a *picrate*, m. p. 218°, and two *platinichlorides*, pale yellow crystals, m. p. 242°, and dark yellow crystals, m. p. 181°: a neutral substance *D*, C_8H_9N , m. p. 85°.

The constitution of the compounds *C* and *D* has not been elucidated. For the structure of *A* and *B*, the following hypothesis

is advanced. Sulphuryl azide decomposes initially into nitrogen and the residue $\cdot N \cdot SO_2 \cdot N \cdot$; the latter then combines with two molecules of *p*-xylene, giving the compound (annexed formula I). This is, however, unstable, and loses



sulphur dioxide, with the production of the univalent radicle (annexed formula II). Two such radicles are unable to unite with one another to yield a ditertiary hydrazine, and re-arrangement of hydrogen atoms consequently occurs between them in accordance



with Wieland's rule, thus leading to the production of the two compounds *A* and *B* (annexed formulae III and IV). The constitution of the compound poorer in hydrogen cannot be regarded as established definitely, since it is possible that the methyl groups play a part in the formation of the new ring; this possibility appears to be excluded in the case of ψ -xylidine (III) by the observation (Schmidt, following abstract) that a completely analogous ψ -aniline is produced from benzene under comparable conditions. The addition of an imino-group to the benzene nucleus with the production of a three- and seven-membered ring has been observed previously in the case of nor-caradienecarboxylic acid. Additional evidence of the existence


of the ring in ψ -xylidine is adduced from the observation

that the substance is gradually decomposed by repeated evaporation with hydrochloric acid, with formation of ammonium chloride.

H. W.

Action of Sulphuryl Azide on Benzene. FRIEDRICH SCHMIDT (*Ber.*, 1922, 55, [B], 1581–1583; cf. Curtius and Schmidt, preceding abstract).—Sulphuryl azide decomposes extremely

slowly when dissolved in boiling benzene, so that continuous ebullition must be maintained for weeks to ensure the decomposition of any considerable proportion of material. This drawback has been overcome by the construction of an autoclave of glass without any metallic contact which permits the boiling point of the solution to be raised to the requisite extent. The product is worked up in the manner described by Curtius and Schmidt in their observations with *p*-xylene. Unexpectedly, the base obtained from the brown, humus-like product of the reaction is uniform; it has the composition C_6H_7N , and is termed ψ -aniline. It is quite distinct from the isomeric picolines. The yields are minimal, so that a complete examination of the new base is impossible. The observation that ammonium chloride is produced when it is repeatedly evaporated with hydrochloric acid indicates the presence

of the  ring. The mechanism of the change is less obvious than in the case of *p*-xylene, since it has not been possible to isolate the "anti-substance" poorer in hydrogen.

ψ -Aniline picrate has m. p. 163° .

H. W.

The Molecular Rearrangement of *s*-Bistriphenylmethylhydrazine. JULIUS STIEGLITZ and RALPH L. BROWN (*J. Amer. Chem. Soc.*, 1922, **44**, 1270—1292).—The authors have repeated and extended the work of Stieglitz and Senior (A., 1917, i, 97). In addition to aniline, which was again isolated after hydrolysing the products of rearrangement of bistriphenylmethylhydrazine caused by heating the substance with anhydrous zinc chloride at 300° , benzophenone was isolated and identified. Triphenylmethylamine could not be found, but this substance itself undergoes decomposition when heated with zinc chloride, giving ammonia, phenyldiphenylmethane, and triphenylmethane, and all these compounds were isolated from the material resulting from heating bistriphenylmethylhydrazine with zinc chloride. These results are taken as supporting the following scheme for the rearrangement of the hydrazine under the experimental conditions,

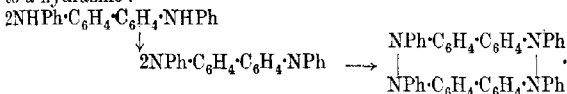
$CPh_3 \cdot NH \cdot NH \cdot CPh_3 \longrightarrow CPh_3 \cdot NH_2 + CPh_3 \cdot N$; $CPh_3 \cdot N \longrightarrow CPh_2 \cdot NPh$, the phenyliminobenzophenone thus formed being hydrolysed to aniline and benzophenone. Quantitative estimations showed that the amount of ammonia or triphenylmethylamine formed is of the order demanded by the above scheme. This series of changes is discussed from the electronic point of view, in which it is considered that the rearrangement is the result of an intramolecular oxidation-reduction which involves a migration of electrons from the methyl carbon to the nitrogen. At the same time, a thermal decomposition proceeds, which is also an intramolecular oxidation-reduction, involving the migration of electrons from the nitrogen to the methyl carbon atom.

It was found that when the rearrangement reaction was carried

out in air, phenol was obtained in quantity, but none was found when the action was carried out in an atmosphere of carbon dioxide. Tentatively, it is suggested that the formation of phenol is due to the capture of oxygen by escaping migrating phenyl radicles, and in support of this view it was found that the sum of the aniline and the phenol obtained was roughly equal to the amount of ammonia formed. Further, it was observed that when bistriphenylmethylhydrazine is heated with zinc chloride in the absence of air there is no rearrangement to an aniline derivative, and there is thus a possibility that the rearrangement described above is the result of an oxidation reaction in which the oxygen of the air takes part.

W. G.

Hydrazines. XXV. A New Class of Ditertiary Aromatic Hydrazines. HEINRICH WIELAND and ALBERT WECKER (*Ber.*, 1922, 55, [B], 1804—1815).—*p*-Phenylenediamines of all types are converted by oxidation in acid solution to quinonedi-immonium salts; the corresponding free bases which have a hydrogen atom attached to the imino-group are reduced by silver oxide or lead dioxide to the di-imines. The reaction is observed, not only with *p*-phenylenediamines but, in principle, with benzidines also. It has, however, been observed by Albert (*Diss.*, Munich, 1916) that *NN'*-diphenylbenzidine behaves in a different manner, giving a product which resembles in composition but differs in molecular weight and properties from the di-imine. This reaction has now been studied more fully and extended to various substituted diphenylbenzidines. It is shown that, as in the case of diphenylamine, the primary product is a radicle with bivalent nitrogen which immediately polymerises to a hydrazine:



The products of the reaction represent a new class of ditertiary aromatic hydrazines; in bromoform solution, they have the simple molecular weight corresponding with the formula, but are polymerised in benzene solution. They are reduced by zinc dust and glacial acetic acid to the benzidines. The colourless bishydrazines dissociate in solution to the coloured radicles, and in this connexion the substituent in the para-position in the benzene nucleus exerts the same influence on the stability of the compound as was observed previously in the case of the tetra-arylhydrazines. Nitric oxide is absorbed readily by the coloured solutions. The radicles, when exposed to a high temperature for some time, exhibit the intermolecular dissociation characteristic of substances containing bivalent nitrogen; the diarylamine is re-formed, whereas the substance poorer in hydrogen has not been identified.

[With T. J. ALBERT].—*NN'*-diphenylbenzidine is oxidised by solid potassium permanganate in the presence of acetone or by silver oxide in the presence of pyridine to *bisdiphenyldibiphenylene*.

*e e**

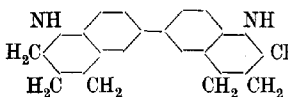
hydrazine, a colourless solid which could not be caused to crystallise. It dissociates in boiling xylene into intensely coloured, brownish-red radicles which re-unite when the solution is cooled. Protracted heating leads to the production of amorphous substances which have not been investigated closely and *NN'*-diphenylbenzidine. When dissolved in hot pyridine, it combines with nitric oxide, yielding diphenylbenzidinebisnitrosoamine, $\text{NO} \cdot \text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NPh} \cdot \text{NO}$, m. p. 158–160° (decomp.), which loses nitric oxide when heated in boiling xylene and regenerates the radicle, which suffers further change to diphenylbenzidine.

Phenyl-*p*-tolylamine is converted by sulphuric acid and sodium dichromate in glacial acetic acid solution and treatment of the product with bisulphite into *NN'*-*di-p*-tolylbenzidine, leaflets, m. p. 233°, which is transformed into the *bishydrazine*, an amorphous compound, m. p. 205° (indefinite). The latter exhibits strongly-marked dissociation in boiling toluene, in which it ultimately becomes converted into *di-p*-tolylbenzidine. The addition of triphenylmethyl could not be effected. On the other hand, the substance unites readily with nitric oxide in the presence of pyridine at 90°, giving the *dinitrosoamine* of *di-p*-tolylhydrazine, slender, yellow needles, m. p. 188–191° (decomp.). Elimination of nitric oxide and production of *di-p*-tolylbenzidine occurs in the same manner as with the derivative of diphenylbenzidine.

NN'-*Di-p*-anisylhydrazine, lustrous crystals, m. p. 226°, is most conveniently oxidised by silver oxide to the corresponding *bishydrazine*, an amorphous, pale-grey powder, m. p. 200° (indefinite). It dissociates more readily than the similar substances described above, thus giving an intensely green solution in warm benzene. At a moderate temperature, it adds nitric oxide with the formation of the *bisnitrosoamine*, $\text{C}_{26}\text{H}_{22}\text{O}_4\text{N}_4$, small, yellow needles, m. p. 160° (decomp.) which loses nitric oxide when heated in boiling toluene.

p-Chlorodiphenylamine, m. p. 74°, is prepared from *p*-chloroacetanilide, bromobenzene, potassium carbonate, and copper powder in boiling nitrobenzene solution, and is converted in the usual manner into *NN'*-*di-p*-chlorophenylbenzidine, lustrous leaflets, m. p. 205°. Dehydrogenation of the latter by potassium permanganate in the presence of acetone gives the corresponding *bishydrazine*, an amorphous substance, m. p. 230° (indefinite). Dissociation of this substance occurs in boiling toluene with the production of a brownish-red solution. The radicle is converted by nitric oxide into the *bisnitrosoamine*, pale yellow needles, m. p. 193° (decomp.).

[With FR. E. HAAS.]—Quinobenzidine (annexed formula) is converted by silver oxide in the presence of pyridine and anhydrous ether into the corresponding *bishydrazine*, a colourless, amorphous powder, m. p. 172° (indefinite). The substance dissociates with difficulty; its solutions in boiling xylene are colourless, but coloured solutions are formed in



boiling ethyl benzoate. It is reduced by zinc dust and concentrated hydrochloric acid in the presence of glacial acetic acid to quinoxalidine.

H. W.

Physico-chemical Studies on Biological Reactions. II. Spectro-chemical Investigations on Amino-acids and Polypeptides. PAUL HIRSCH and RUDOLF KUNZE (*Fermentforsch.*, 1922, 6, 30—55).—By means of the Pulfrich refractometer and the Löwe interferometer, the authors have investigated the refractions of a number of amino-acids and polypeptides with the view of obtaining data by means of which scission of polypeptides or proteins into their constituent amino-acids, as well as the reverse reactions, may be investigated.

T. H. P.

The Natural Proteins. I. Behaviour of Chlorine Dioxide towards Organic Substances. ERICH SCHMIDT and KARL BRAUNSDORF (*Ber.*, 1922, 55, [B], 1529—1534; cf. Schmidt and Graumann, A., 1921, i, 912; Schmidt and Duysen, this vol., i, 206).—The behaviour of substances closely allied to the natural proteins towards chlorine dioxide has been investigated by the method described previously (Schmidt and Graumann, *loc. cit.*) except that it has been found advisable to alter the order of addition of the reagents in the final titration, 3 c.c. of 2-N-sulphuric acid, followed by 1.5 c.c. of 2-N-aqueous potassium iodide solution and 2—3 c.c. of water being run into the liquid in the given sequence. The substances are considered to be stable towards the reagent when the chlorine dioxide content of the solution is not diminished by more than 2% after periods of twenty-four, forty-eight, or seventy-two hours. The following substances are stable: amino-acids and their derivatives (urethane, glycine, glycine hydrochloride, ethyl aminoacetate hydrochloride, aminoacetonitrile sulphate, glycineamide hydrochloride, phenylaminoacetic acid, hippuric acid, betaine, betaine hydrochloride, creatine, alanine, phenylalanine, valine, leucine and its hydrochloride, aspartic acid, asparagine, glutamic acid, serine, hydroxyproline, taurine, glycylglycine hydrochloride, leucylglycine, triglycine); amines and their derivatives (tetramethylenediamine hydrochloride, pentamethylenediamine hydrochloride, α -aminopropane- β -ol oxalate, guanidine hydrochloride, tetramethylammonium chloride, choline hydrochloride); amides and their derivatives (acetamide, chloroacetamide, propionamide, phenylacetamide, *s*-dimethyloxamide, carbamide, biuret, hydantoin); imides (glutarimide, phthalimide); polyhydroxy-alcohols (ethylene glycol, glycerol, mannitol, carbohydrates, inositol); mono- and poly-basic acids, esters (acetic acid, chloroacetic acid, stearic acid, benzoic acid, oxalic acid, adipic acid, trilaurin, tristearin, α -crotonic acid, maleic acid and its anhydride, fumaric acid); hydroxy-acids, esters (ethyl lactate, tartaric, citric, and quinic acids); nitriles (acetonitrile, benzonitrile, succinonitrile); cyclic compounds (benzene, naphthalene, cyclohexane, pyridine sulphate, quinoline hydrochloride, piperidine hydro-

chloride, β -nitroanethole). The following substances are attacked by chlorine dioxide: amino-acids and derivatives (tyrosine, *N*-benzoyltyrosine, 3:4-dihydroxyphenylalanine, tryptophan, histidine hydrochloride, cystine); mono- and poly-hydroxyphenols; unsaturated carbon compounds (*cyclohexene*, allyl alcohol, anethole, cinnamyl alcohol, cinnamaldehyde, oleic acid, triolein, uric acid, furfuraldehyde, indole, β -methylindole); carbon-sulphur compounds (mercaptans, dialkyl disulphides, compounds such as thiocarbamide).

Histologically, a solution of chlorine dioxide in acetic acid is found to be very useful for the removal of stains due to melanins from tissues without in the least affecting their anatomical features.

H. W.

Yeast-nucleic Acid. III. H. STEUDEL and E. PEISER (*Z. physiol. Chem.*, 1922, **120**, 292—295).—Guanylic acid can be obtained from yeast-nucleic acid when the sodium salt of the latter is treated with dilute sodium hydroxide solution. The guanylic acid portion of the molecule can thus be completely removed if the reaction takes place at the ordinary temperature. No guanylic acid is removed when the manipulation is carried out at 0°.

S. S. Z.

The Dissolution of Gelatin. FRED FAIRBROTHER and ENOCH SWAN (*T.*, 1922, **121**, 1237—1244).

The Sol-Gel Equilibrium in Protein Systems. ROBERT HERMAN BOGUE (*J. Amer. Chem. Soc.*, 1922, **44**, 1313—1322).—Viscosity-plasticity relations of solutions of gelatin of different concentrations and over a temperature range from 25° to 60° have been studied by measurements with a MacMichael torsional viscometer. The results indicate that gelatin in aqueous solution follows the laws of viscous flow at the higher temperatures and has the properties of plastic flow at lower temperatures. The transition between the sol and gel form does not take place at any definite temperature, but extends throughout a rather indefinite period of temperature. Further it was found that, at a given temperature, the increase or decrease in viscosity with time was dependent on the hydrogen-ion concentration, the nature of the inorganic ions present, and the amount of hydrolysed protein in the system. It is considered that the viscosity of pure gelatin at any given hydrogen-ion concentration is inversely proportional to some function of the temperature, and that, at equilibrium, there will be some viscosity which will correspond with every point of temperature.

W. G.

The Structure of Elastic Gels. ROBERT HERMAN BOGUE (*J. Amer. Chem. Soc.*, 1922, **44**, 1343—1356; cf. preceding abstract and *Chem. Met. Eng.*, 1920, **23**, 61).—The author restates his theory as to the catenary or fibrillar structure of gelatin-water systems and quotes further work and contemporary investigations

in support of this hypothesis and further postulates. According to this theory, the sol consists of slightly hydrated or swollen molecules united into short chains. When the temperature falls the threads increase in length and number, and their power of water absorption increases, resulting in an increase in viscosity. A solid jelly results when the relative volume occupied by the swollen molecular threads has become so great that freedom of motion is lost, and the adjacent heavily swollen aggregates cohere. The rigidity is dependent on the relative amount of free solvent in the interstices of the aggregates, and on the amount of solvent that has been taken up by the gelatin in a hydrated or imbibed condition. The resiliency or elasticity is dependent on the length and number of the catenary threads. Solution is the reverse of gelation and the swelling is determined by osmotic forces and the Donnan equilibrium.

The results of a study of the influence of electrolytes, of varying hydrogen-ion concentration, and of the valency of the combining ion on several of the characteristic properties of gelatin, namely, swelling, viscosity, jelly consistency, foam, turbidity, and alcohol number, give additional support to the theory. Smith's data on mutarotation (cf. *J. Ind. Eng. Chem.*, 1920, **12**, 878) are in accord with the theory, as is Loeb's occlusion theory. W. G.

Action of Alum on Animal Glue. A. GUTBIER, E. SAUER, and F. SCHELLING (*Kolloid Z.*, 1922, **30**, 376—395).—Treatment of glue by alum brings about two actions, a strong increase in the viscosity without any visible change and at a higher temperature in faintly acid solutions the formation of a precipitate. The addition of alum to both bone and leather glue immediately reduces the colour. The sensitiveness of glue to alum varies with the different varieties, thus the viscosity of leather glue is increased by very small concentrations of alum, whilst very large concentrations are necessary to give a noteworthy increase of viscosity with bone glue. At higher temperatures, in the case of leather glue there is a continuous decrease in the viscosity, depending on the concentration of the alum and the time during which the two substances have been in contact. Bone glue is much more stable than leather glue to high temperatures and to alum. The basic aluminium compounds and aluminium hydroxide which are present in colloidal form in alum solution have a specific action on glue, and, further, the hydrogen ion, due to hydrolysis, also has a specific action. Glue jellies mixed with alum on dialysis allow all the other constituents of the alum to be removed, but hold the aluminium back quantitatively. The precipitates produced during the clarification of glue by alum and phosphoric acid contain both glue and aluminium in varying proportions, and belong to the group of adsorption compounds; they have a considerable surface energy and consequently possess a great clarifying power. The more rapidly the precipitate forms, the greater is its clarifying power.

After a correctly carried out clarification, the glue contains only small quantities of aluminium, but it contains the whole of the acid added. The clarification of glue is accompanied always by a deterioration, as shown by the decrease in the viscosity. This is not due directly to the clarification process, but to secondary reactions. The acid added and the prolonged heating bring about hydrolysis which yields substances that are not glue-like. Leather glue is more sensitive than bone glue in this respect. J. F. S.

The Composition of Silk Fibroin and its Structure.

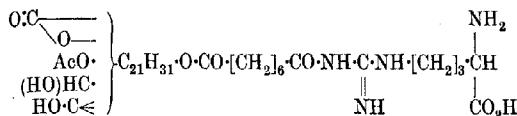
EMIL ABDERHALDEN (*Z. physiol. Chem.*, 1922, 120, 207—213).—One hundred parts of ash-free silk fibroin yielded 25 of *d*-alanine, 2.5 of *l*-leucine, 1.5 of phenylalanine, 1.8 of *l*-serine, and 1 of *l*-proline. Altogether 86.4% of the amino-acids were accounted for. The examination of products in the intermediate stages of the process of hydrolysis showed the presence of considerable quantities of *d*-alanyl-glycine anhydride m. p. 240—247°, $[\alpha]_D -5.02^\circ$, small quantities of glycyl-*l*-tyrosine anhydride, and a compound containing serine, *d*-alanine, and glycine. S. S. Z.

The Protamines. R. EBERHARD GROSS (*Z. physiol. Chem.*,

1922, 120, 167—184).—When clupeine is heated for eighty minutes with 4 vol. % sulphuric acid at 160°, it loses the property of giving the biuret reaction. The hydrolysed product contains arginine, and monoamino-acids as well as a dipeptide-like compound consisting of a combination of at least two arginine molecules. By precipitating with phosphotungstic acid in alcoholic solution, it is possible to separate free arginine from the arginine peptide. The author confirms Nelson-Gerhardt's deduction (*A.*, 1919, i, 503) that in clupeine the monoamino-acids are linked together. S. S. Z.

The Poisonous Substance of Toads. HEINRICH WIELAND

and RICHARD ALLES (*Ber.*, 1922, 55, [B], 1789—1798; cf. Wieland and Weil, *A.*, 1913, i, 1343).—Further attempts to isolate the poisonous material from the skin of the toad have led to an unexpected result, since a more careful repetition of methods that were previously successful did not lead to the isolation of bufotalin. It now appears that this is not present as such, but is a product of the decomposition of the actual poison, *bufotoxin*, $C_{40}H_{62}O_{11}N_4$, m. p. 204—205° (decomp.). The isolation of the latter from the extract of the skins and from the secretions of the glands is described in detail. Bufotoxin is readily reduced by hydrogen in alcoholic solution in the presence of palladium black to *hydrobufotoxin*, $C_{40}H_{64}O_{11}N_4$, slender needles, m. p. 187°. Bufotoxin is readily hydrolysed by mineral acids to bufotalein and suberylarginine; the latter could not be caused to crystallise, but its composition is established by hydrolysing it with more concentrated acid to suberic acid and arginine. The constitution of bufotoxin may be resolved as follows:



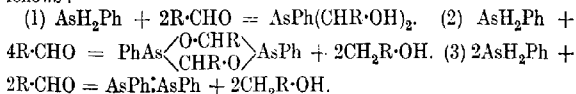
Its conversion into bufotalin is expressed by the scheme: $\text{C}_{26}\text{H}_{37}\text{O}_8 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_{13}\text{H}_{25}\text{O}_3\text{N}_4 = \text{C}_{26}\text{H}_{36}\text{O}_6$ (bufotalin) + $\text{C}_{14}\text{H}_{26}\text{O}_5\text{N}_4$, whereas its hydrolysis by dilute hydrochloric acid takes place in accordance with the equation: $\text{C}_{40}\text{H}_{62}\text{O}_{11}\text{N}_4 \rightarrow \text{C}_{24}\text{H}_{30}\text{O}_3$ (bufotalin) + $\text{C}_{14}\text{H}_{26}\text{O}_5\text{N}_4 + \text{CH}_3 \cdot \text{CO}_2\text{H} + \text{H}_2\text{O}$.

Acetylbufotalin is converted by concentrated hydrochloric acid into acetylbufotalin, $\text{C}_{26}\text{H}_{32}\text{O}_4$, which is identical with the product obtained by Wieland and Weil (*loc. cit.*) by the acetylation of bufotalin. Catalytic hydrogenation of acetylbufotalin in the presence of platinum black leads to the formation of acetylbufotalan, $\text{C}_{26}\text{H}_{40}\text{O}_4$, aggregates of needles, m. p. 165°. H. W.

Physico-chemical Studies on Biological Reactions. I. PAUL HIRSCH (*Fermentforsch.*, 1922, 6, 27—29).—The author is proposing to employ physico-chemical methods, particularly optical methods, for the investigation of the problems of enzymes and immuno-chemistry. T. H. P.

Dependence of the Action of Succinodehydrogenase on Hydrogen-ion Concentration. ERIK OHLSSON (*Skand. Arch. Physiol.*, 1921, 41, 77—100; from *Chem. Zentr.*, 1922, i, 58 (cf. this vol., i, 792, and Widmark, A., i, 600).—Succinodehydrogenase prepared from horse muscle has as optimum conditions P_{H} 8.7 and 45°. Higher temperatures depress activity. The enzyme is inactive at 55°. The velocity of reaction is independent of the concentration of the reacting substances, provided they are present in minimal amount. G. W. R.

The Reactions of the Arsines. II. Condensation of Aromatic Primary Arsines with Aldehydes. CHARLES SHATTUCK PALMER and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1922, 44, 1356—1382; cf. A., 1921, i, 70).—Primary arylarsines and aldehydes react in three ways, depending on the conditions of the reaction, as follows:—



Aromatic primary arsines and aliphatic aldehydes condense in the presence of concentrated hydrochloric acid at room temperature to give compounds of the type $\text{AsPh}(\text{CHR} \cdot \text{OH})_2$. With aromatic aldehydes, it is best to use dry hydrogen chloride, with or without a solvent.

Details are given for preparing phenylarsinic acid and phenylarsine on a large scale, and from the latter the following compounds

are prepared. Phenylarsine has d_{25}^{25} 1.349, n_D^{25} 1.6082. *Phenyldi- α -hydroxyethylarsine*, $\text{AsPh}(\text{CHMe}\cdot\text{OH})_2$, has b. p. 175—176°/22 mm., d_{25}^{25} 1.252, n_D^{25} 1.5619, giving a *platinichloride*, m. p. 169—170°. *Phenyldi- α -hydroxy-n-propylarsine*, b. p. 196—197°/24 mm., d_{25}^{25} 1.176, n_D^{25} 1.5425 giving a *platinichloride*, m. p. 148—149°. *Phenyldi- α -hydroxy-n-butylarsine*, b. p. 187°/10 mm., d_{25}^{25} 1.116, n_D^{25} 1.5271 giving a *platinichloride*, m. p. 119—121°. *Phenyldi- α -hydroxyisovalerylarsine*, b. p. 170°/6 mm., m. p. 62°, d_{25}^{25} 1.079, n_D^{25} 1.5202 giving a *platinichloride*, m. p. 84—85°. *Phenyldi- α -hydroxy-n-heptylarsine*, b. p. 263—264°/2 mm., d_{25}^{25} 1.069, n_D^{25} 1.4650. *Phenyldi- α -hydroxy-p-chlorobenzylarsine*, m. p. 164°. *Phenyldi- α -hydroxy-p-methoxybenzylarsine*, a yellow oil. *Phenyldi- α -hydroxy-o-carbomethoxybenzylarsine*, m. p. 145—147°.

[With W. A. CAROTHEES.]—*p-Chlorophenylarsine*, m. p. 30.5—30.7°; b. p. 116°/33 mm., 159°/200 mm.; d_{25}^{25} 1.507, n_D^{25} 1.6143 gives *p-chlorophenyldi- α -hydroxybenzylarsine*, m. p. 218—218.5°, and *p-chlorophenyldi- α -hydroxyethylarsine*, b. p. 183°/23 mm.; d_{25}^{25} 1.336; n_D^{25} 1.5728.

[With E. E. PARKS.]—*o-Chlorophenylarsine*, b. p. 206°, d_{25}^{25} 1.519, n_D^{25} 1.6250, obtained from *o-chlorophenylarsinic acid*, m. p. 186—187°, gives *o-chlorophenyldi- α -hydroxybenzylarsine*, m. p. 146—147°.

[With G. O. BURR.]—*p-Tolylarsine*, b. p. 113.5°/44 mm., m. p. 20°, d_{25}^{25} 1.295, n_D^{25} 1.5891, gives *p-tolyldi- α -hydroxybenzylarsine*, m. p. 208° and *p-tolyldi- α -hydroxyethylarsine*, b. p. 176—177°/22 mm., d_{25}^{25} 1.2331, n_D^{25} 1.5570.

[With J. S. PIERCE.]—*o-Tolylarsine*, b. p. 121°/93 mm., d_{25}^{25} 1.301; n_D^{25} 1.5925, gives *o-tolyldi- α -hydroxybenzylarsine*, m. p. 140° and *o-tolyldi- α -hydroxyethylarsine*, b. p. 165°/21 mm., d_{25}^{25} 1.244, n_D^{25} 1.5573.

Many of these compounds oxidise slowly in the air with the formation of an arsenic acid and aldehyde. The process is more rapid in the presence of a solvent such as carbon tetrachloride. With oxidising agents, halogens, phosphorus pentachloride and phenylarsenious chloride these compounds behave exactly as if they were a mixture of phenylarsine and aldehyde. The aliphatic derivatives may be titrated quantitatively in ethereal solution with iodine, the following reaction occurring: $\text{C}_6\text{H}_5\text{As}(\text{CHR}\cdot\text{OH})_2 + 2\text{I}_2 \longrightarrow \text{AsPhI}_2 + 2\text{HI} + 2\text{R}\cdot\text{CHO}$.

The compounds form unstable additive products with halogen acids and stable additive compounds with chloroplatinic acid. They are decidedly stable towards reducing agents and towards certain dehydrating agents. They do not react with Grignard reagents. With certain dehydrating agents such as acetyl chloride, acetic anhydride, or even anhydrous hydrogen chloride, they react to give tetrahydro-1:4:2:5-dioxadiarsines as shown in equation (2) above. These compounds are also obtained directly from primary aromatic arsines and aldehydes by leaving the mixture for two days in the presence of anhydrous hydrogen chloride; the following are described. 2:5-Diphenyltetrahydro-1:4:2:5-dioxadiarsine, b. p. 215

—216°/9 mm., d_{25}^{25} 1.547, n_D^{25} 1.6522. 2:5-Diphenyl-3:6-dimethyl-tetrahydro-1:4:2:5-dioxadiarsine, b. p. 257°/10 mm., d_{25}^{25} 1.369, n_D^{25} 1.6332, giving a *platinichloride*, m. p. 130—131°, and a *cuprichloride*, m. p. 150—152°. 2:5-Diphenyl-3:6-diethyltetrahydro-1:4:2:5-dioxadiarsine, b. p. 212°/2 mm., d_{25}^{25} 1.336, n_D^{25} 1.6217. 2:5-Diphenyl-3:6-di-n-propyltetrahydro-1:4:2:5-dioxadiarsine, b. p. 241—242°/2 mm., d_{25}^{25} 1.297, n_D^{25} 1.5856. 2:5-Diphenyl-3:6-di-isobutyltetrahydro-1:4:2:5-dioxadiarsine, b. p. 240°/16 mm., d_{25}^{25} 1.296, n_D^{25} 1.5869, giving a *platinichloride*, m. p. 76—77°, and a *cuprichloride*, m. p. 78—79°. 2:5-Diphenyl-3:6-difuryltetrahydro-1:4:2:5-dioxadiarsine. The tetrahydrodioxadiarsines oxidise in the air ~~to~~ give arylarsine oxides and aldehydes. With iodine and phosphorus pentachloride, products are obtained which might be expected from a mixture of arylarsine and aldehyde.

The reaction of type (3) given above occurs when a mixture of an aromatic primary arsine and an aromatic aldehyde is left at room temperature without a catalyst or if the mixture is heated with or without a catalyst.

W. G.

Physiological Chemistry.

Surface Reactions in Living Cells. O. WARBURG (*Z. Elektrochem.*, 1922, 28, 70—75).—The processes of breathing and assimilation by living cells has been investigated in the case of red blood-corpuses, and bacterial and plant cells in various circumstances. The rate of oxidation of cystine, and that of assimilation, in the presence of narcotics has been investigated, and the quantity of narcotic determined, in the case of alcohols, urethanes, ketones, nitriles, and substituted carbamides, which is necessary to reduce the assimilation by 50%. The quantity of narcotic decreases rapidly from member to member in an homologous series, thus a solution of methyl alcohol containing 5 mols. per litre cuts down the breathing and assimilation by 50%, whilst 0.045 mol. per litre of amyl alcohol has the same effect. The following hypothesis of the surface action of living cells is put forward. The surface of the solid cell constituents is to be regarded as a mosaic of regions poor in iron and rich in iron, of which those poor in iron are the most abundant. Both the metal-containing and metal-free areas adsorb dissolved substances from the cell fluids, and in general to the same extent. Hydrocyanic acid, on account of its affinity for the heavy metals, is mainly adsorbed on the metal-containing areas. Consequently the seat of the chemical processes, breathing and assimilation, is the iron-containing surface. When hydrocyanic acid is brought into a

living cell, its effect is to displace the reacting substances from the iron-containing regions and so stop assimilation and breathing. Very little hydrocyanic acid is sufficient to achieve this, since the metal-containing areas constitute only a small fraction of the whole surface. For the same reason, the displacement from the metal-containing areas leads to no noticeable reduction in the total amount of adsorbed substance. Consequently, the action of hydrocyanic acid depends on specific adsorption and displacement. Narcotics displace the reacting substances from both regions and to the same extent, and so stop breathing and assimilation, but in this case the whole surface must be covered with the displacing substance. The quantity of narcotic necessary to produce the same effect on assimilation and breathing is therefore extremely large in comparison with the amount of hydrocyanic acid. Hence it may be stated that the cause of the acceleration of reactions in living cells is the adsorption in iron-containing parts of the surface. J. F. S.

The Rôle of Vitamins in the Chemistry of the Cell.

W. R. HESS (*Z. physiol. Chem.*, 1922, **120**, 277—280).—Polemical in reply to Abderhalden (this vol., i, 607).

The Action of Whole Blood on Acids. ERNEST LAURENCE

KENNAWAY and JAMES MCINTOSH (*Biochem. J.*, 1922, **16**, 380—386).—If sulphuric acid (0.01N) containing 0.9% of sodium chloride be shaken with whole blood, and the mixture centrifuged, about 80% of the acid is removed, so that it is no longer titrable in the fluid. If acid be added to plasma, the amount neutralised is approximately constant for a given amount of plasma, and does not vary with the amount of acid used. On the other hand, the resulting P_H in the two cases is approximately the same for a given ratio of acid to blood, the plasma showing a rather greater acidity. Laked blood does not appear to neutralise so efficiently as whole blood, and so the action of the latter seems to be due to some form of adsorption, dependent on the structure of the corpuscles. W. O. K.

Carbonic Acid Compounds and Hydrogen-ion Activities in Blood and Salt Solutions. ERIK JOHAN WARBURG (*Biochem. J.*, 1922, **16**, 153—340).

—This comprehensive paper deals with the equilibrium of dissolved substances in homogeneous and heterogeneous media, with particular reference to the theories of Bjerrum and of Donnan. The general theoretical results are applied to elucidate the carbon dioxide equilibrium and the hydrogen-ion concentration in blood and also the development of a modified Henderson-Hasselbach equation. For the mathematical and experimental investigations and results, the original must be consulted. The paper includes valuable reviews of previous work. W. O. K.

Calcium in the Blood of various Species of Animals.

P. MAZZOCCO (*Anal. Assoc. Quim. Argentina*, 1921, **9**, 313—325).—The method of Halverson and Bergeim (*A.*, 1918, i, 50) is modified

by using trichloroacetic acid (cf. Lyman, A., 1917, ii, 271) instead of sodium picrate to precipitate albumins. An improved method of washing the precipitate of calcium oxalate by decantation is described. Data are given for the calcium content of entire blood, plasma, corpuscles, and serum for different species of animals. The calcium content of the blood constituents of the same animal species is very constant. Calcium occurs, although in small amounts, equally in nucleated and non-nucleated red corpuscles. The calcium content of plasma is practically identical with that of serum. G. W. R.

Does Cyanic Acid Exist in the Blood? MAURICE NICLOUX and GEORGES WELTER (*Compt. rend.*, 1922, **174**, 1733—1735).—The authors find no indication of the presence of cyanic acid either in blood or lymph in the normal state. W. G.

Blood Sugar. II. Alimentary Hyperglycæmia under Normal and Pathological Conditions. MAX ROSENBERG (*Arch. exp. Path. Pharm.*, 1922, **93**, 208—240).—A comparative analysis of the type of curves obtained by estimating the sugar of the blood at intervals after the oral administration of 100 grams of dextrose in normal individuals, in diabetes and in hyperthyroidism.

C. R. H.

Creatine and Creatinine Metabolism. IV. The Question of the Occurrence of Creatinine and Creatine in Blood. JEANETTE ALLEN BEHRE and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1922, **52**, 11—33).—In the estimation of creatinine in blood filtrates by Folin's method (A., 1914, ii, 505) the coloration produced with picric acid is due to a substance which differs from creatinine in two respects; it is not adsorbed by kaolin from acid solutions, neither is it destroyed by boiling with alkalis. The amount of chromogenic substance present in the blood increases when the kidney function is impaired, and, in this case, it is to some extent adsorbed by kaolin and destroyed by alkalis. Nevertheless, it was found impossible to isolate creatinine from such bloods, although small quantities of added creatinine were recovered almost quantitatively in the form of the zinc chloride compound. It is thus improbable that creatinine is present in blood in more than minute amounts.

The creatine content of blood is best estimated by a method similar to that used for urine (A., 1914, ii, 688). The preliminary conversion into creatinine must not be effected by heating with picric acid, since, under these conditions, picric acid reacts with blood to give a product yielding colour on addition of alkali. The blood of dogs with impaired kidney function showed a high creatine content; this suggests that blood creatine is a waste product which is eliminated by the kidney in the form of creatinine or of some other substance. E. S.

The Relation of Salivary to Gastric Secretion. TOMOICHI NAKAGAWA (*Biochem. J.*, 1922, **16**, 390—393).—Boiled potato

starch inhibits the action of the pepsin and accelerates the action of the rennin of the natural gastric juice, but not after being acted on by fresh human saliva. Saliva has a delaying action of its own on the clotting of milk. W. O. K.

Intestinal Intoxication. I. The Presence and Significance of Histamine in an Obstructed Bowel. R. W. GERARD (*J. Biol. Chem.*, 1922, 52, 111—124).—The presence of histamine in the fluid contained in closed loops of the large and small intestine of dogs was indicated qualitatively by its depressant action when injected intravenously in dogs, and by its action on strips of the intestine of a guinea pig. Estimations by the method of Hanke and Koessler (A., 1920, ii, 784) gave average values corresponding with 2 to 3 mg. of the dihydrochloride per 100 c.c. of fluid. Evidence was also obtained of the presence of a histamine derivative of a peptide nature. No histamine was found in the sterile secretion of jejunum, although it was present in the sterile mucosa. Loop fluid and mucosa also contain histidine. E. S.

The Oxidising Enzymes in the Phenomena of Life in its Normal and Pathological States. G. MARINESCO (*Bul. Soc. Chim. Romania*, 1922, 4, 3—12).—A more detailed account of work already published (A., 1920, i, 130). W. G.

Decomposition of Proteins of Organs. K. THOMAS (*Festschr. K. Wilhelm Ges. Förd. Wiss. Zehnjährigen Jubiläum.*, 1921, 205—207; from *Physiol. Abstr.*, 1922, 7, 187).—Organ protein undergoes in the body changes which are different from those undergone by protein introduced in the food. For example, arginine is regularly formed from organ protein during minimum nitrogen excretion, whereas it is not formed from food protein. The amino-acids in the organ protein can apparently undergo chemical changes without cleavage of the peptide linking. W. O. K.

Origin and Destiny of Cholesterol in the Animal Organism. XIII. The Autolysis of Liver and Spleen. JOHN ADDYMAN GARDNER and WILLIAM FOX (*Proc. Roy. Soc.*, 1922, [B], 93, 486—492).—The autolysis under aseptic conditions of liver and spleen is not accompanied by increase in the amount of cholesterol present. It is unlikely therefore that either of these organs is concerned with the synthesis of cholesterol in the body. C. R. H.

The Permeability of the Glomerulus Membrane for Stereoisomeric Sugars. H. J. HAMBURGER (*Berlin Klin. Woch.*, 1922, 1, 418; from *Physiol. Abstr.*, 1922, 7, 192).—The permeability of the membrane is not related to the size of molecule of the sugar, but to its configuration; thus lactose goes through although its molecule is twice the size of that of dextrose, which does not; *d*-galactose consists of α - and β -modifications, one of which passes; the other does not. The same is true for α - and β -xylose. W. O. K.

The Influence of Adrenaline on the Permeability of the Limiting Membrane of Muscle Fibres. HERMANN LANGE (*Z. physiol. Chem.*, 1922, **120**, 249—266).—It has been ascertained by chemical and physiological methods that adrenaline possesses the property of diminishing the permeability of the limiting membrane of the muscle fibres of the frog. S. S. Z.

Continuous Current and Permeability (in Muscle). II. Effect of Alkaloidal Salts and Other Organic Electrolytes. JOSEPH VORSCHÜTZ (*Pflüger's Archiv*, 1921, **190**, 54—65; from *Chem. Zentr.*, 1922, i, 3).—A continuation of work on the electrical effect of substances on muscle. Strychnine, pilocarpine, codeine, and brucine salts are electrically indifferent: atropine, cocaine, and morphine salts react electronegatively. Quinine, optochin, and caffeine salts, and to a lesser degree cinchonine salts, develop a strong continuous current. These alkaloids, which are muscle poisons, probably exert their effect on muscle by means of the free bases liberated by hydrolysis. Salts of quaternary ammonium bases, sodium salts of the lower fatty acids, sodium salicylate, and sodium benzoate are almost without effect or react slightly electronegatively. The effect is independent of the length of the carbon chain. G. W. R.

The Physiology of Creatine. OTTO RIESSER (*Z. physiol. Chem.*, 1922, **120**, 189—206).—Although the total creatine-content of the mixed skeletal muscles of the rabbit is always the same, those of the various muscles differ from one another by amounts depending on the rate of contraction. Parallelism exists between the creatine and the lactacidogen contents of the various muscles. This parallelism does not persist when the condition of the muscles is altered by various factors. The author cannot confirm R. Kahn's observations (*Pflüger's Archiv*, 1919, **177**, 294). S. S. Z.

The Effect of Cold Storage on the Carnosine Content of Muscle. WINIFRED MARY CLIFFORD (*Biochem. J.*, 1922, **16**, 341—343).—Using the colorimetric method previously described (Clifford, A., 1921, ii, 604), it has been found that the carnosine content of meat decreases during cold storage. W. O. K.

Influence of Minute Concentrations of Acid and Alkali on the Blood-vessels and other Smooth Muscle. PAUL HEYMANN (*Arch. expl. Path. Pharm.*, 1922, **90**, 27—76).—The existing literature dealing with the physiological action of acid and alkali on smooth muscle is reviewed at some length. A long series of experiments, performed for the most part by the perfusion of the blood-vessels of frogs or of surviving rabbits' ears, is described. The effect on the rate of flow of the perfusion fluid caused by the addition of small amounts of acid and alkali was investigated, and some experiments were also carried out on isolated strips of smooth muscle. It was found that concentrations

of acid or alkali of the order of $N/1000$ cause marked vaso-constriction; this is antagonised by sodium nitrite and by hypertonic salt and sugar solutions. The effect was obtained both with Ringer's solution and with serum as the original perfusion fluid. Simultaneously with the vaso-constriction, there appears marked oedema, the formation of which is, however, apparently dependent on the particular acid employed; those acids (sulphuric and phosphoric) which have the weakest vaso-constrictor effect produce the greatest oedema.

The constrictor effect of adrenaline is abolished or reversed during perfusion with acid fluids; it is unaffected by alkalis.

In physiological salt solution (free from calcium), lactic acid and carbon dioxide cause vaso-dilatation. Isolated smooth muscle is stimulated by small and inhibited by large concentrations of acid and alkali. Alkalis act directly on the muscle alone; acids also act on the nervous apparatus, which they first stimulate and then inhibit.

C. R. H.

Action of Muscle Tissue on Fumaric, Maleic, Glutaconic, and Malic Acids. H. D. DAKIN (*J. Biol. Chem.*, 1922, **52**, 183—189).—By the action of muscle enzymes, fumaric acid is converted into *l*-malic acid and not into *i*-malic acid, as stated by Einbeek (*A.*, 1919, **1**, 467). Maleic acid, under the same conditions, gives no trace of malic acid; glutaconic acid, however, is to a small extent converted into β -hydroxyglutamic acid. When *i*-malic acid is submitted to the action of muscle tissue, the *l*-*iso*-component is preferentially consumed and is converted, to some extent, into fumaric acid. The *bisphenylhydrazide* of *i*-malic acid, colourless prisms, m. p. 221—224° (uncorr.), has been prepared. E. S.

Spontaneous Reducing Effect of Muscle on Methylene-blue. Physiology of Dehydrogenases. GUNNAR AHLGREN (*Skand. Arch. Physiol.*, 1921, **41**, 1—30; from *Chem. Zentr.*, 1922, **i**, 58; cf. Widmark, *A.*, **1**, 600).—By the agency of dehydrogenases occurring in muscle, hydrogen is abstracted from certain substances, called hydrogen "donators," and added to methylene-blue, which is changed thereby to the leuco-base. Methylene-blue, acting as hydrogen acceptor, thus plays the same physiological rôle as oxygen. Substances which can act as hydrogen donators have specific dehydrogenases. The reducing power of muscle is estimated by determining the time required for decolorisation of known amounts of methylene-blue. The red muscle of rabbits and doves has greater reducing power than white muscle. Heart muscle has greater reducing power than skeletal muscle. Seasonal variation in reducing power of frog muscle was observed with a summer maximum and a winter minimum. Reducing power is greatest in mammalian muscle. The lowest reducing power is shown by the muscle of worms.

G. W. R.

Alligator and Crocodile Oils. SHŪMEI KOBAYASHI (*J. Chem. Ind., Japan*, 1922, **25**, 691—703).—An alligator oil

obtained from *Alligator mississippiensis* from North America is a light yellow liquid of peculiar fishy odour (d_4^{25} 0.9285 and n_D^{20} 1.4795). Arachidonic, clupanodonic, oleic, and palmitic acids, and a new acid of the $C_nH_{2n-6}O_2$ series were detected in the saponification product of the oil. The new acid, $C_{22}H_{36}O_2$, has n_D^{20} 1.4888 and iodine value 308.0, and on hydrogenation gives an acid of m. p. 76–76.5°. A crocodile oil obtained from *Crocodilus niloticus* from Africa is a solid fat at room temperature (d_4^{20} 0.8989, n_D^{20} 1.4602, iodine value 60.3). It is mainly composed of almost equal amounts of oleic and stearic esters, a small amount of highly unsaturated acid esters being also present.

K. K.

The Dyes from *Purpura aperta* and *Purpura lapillus*. P. FRIEDLÄNDER (*Ber.*, 1922, 55, [B], 1655–1658).—The dye obtained from *Purpura aperta* appears to be identical with 6:6'-dibromo-indigotin in so far as elementary analysis, solubility, dyeing capacity, and absorption spectrum allow a judgment to be formed. A more complete comparison of the natural and synthetic products was impossible by reason of the limited amount of dye available. The dye from *Purpura lapillus* appears to be identical with dibromo-indigotin, but the amount of material was too small to permit an elementary analysis.

H. W.

Comparative Spectroscopic Study of the Green Pigment of the *Chetoptera* and of the Chlorophyll of the *Ulva*. MARC ROMIEU and FERNAND OBATON (*Compt. rend.*, 1922, 175, 51–54).—The spectra of chetopterin, the green pigment of *Chetoptera* and of the chlorophyll of *Ulva* coincide almost exactly, and thus indicate the relationship of the two pigments. Chetopterin is thus a pigment of extrinsic origin, which must be placed in the group of enterochlorophylls.

W. G.

The Origin of Creatine and Creatinine. H. STEUDEL and R. FREISE (*Z. physiol. Chem.*, 1922, 120, 244–248).—The intravenous injection of the sodium salt of nucleic acid and of histidine in the dog did not alter the creatinine content of the urine. It was, however, observed in some of these experiments that the injection influenced the metabolic process.

S. S. Z.

Sulphohæmoglobinæmia. A. A. HIJMAN VAN DEN BERGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, 23, 1392–1398).—In the blood of a certain percentage of healthy rabbits and in that of human beings suffering from intestinal stasis, spectroscopic evidence is obtained of the presence of sulphohæmoglobin. Combined estimations of the available hæmoglobin by Barcroft's method and of the iron-content by the titanium method show that as much as 20% of the total hæmoglobin may be in the form of the sulphur compound. Sulphohæmoglobinæmia is not associated with the presence of demonstrable amounts of hydrogen sulphide in the blood serum.

C. R. H.

The Composition of the Scales in Psoriasis. EMIL ARDERHALDEN and BERNHARD ZORN (*Z. physiol. Chem.*, 1922, **120**, 214—219).—On extracting 9.2742 grams of the dry scales with carbon tetrachloride in a Soxhlet apparatus 0.6894 gram was obtained of a fraction containing 0.00075 of phosphorus. The extracted residue contained 0.0233 of phosphorus. The moisture varied from 7.45 to 9.5%. The average ash content of dry scales was found to be 1.185%. The following amino-acids were established in the substance:—Alanine 4.5%, serine 0.78%, cystine 1.85%, valine 3.25%, leucine 5.25%, glutamic acid 6.5%, phenylalanine 2.32%, tyrosine 3.25%, and proline 3.05%. S. S. Z.

The [Physiological] Action of Mercury. WILLIAM SALANT and NATHANIEL KLEITMAN (*J. Pharm. Expt. Ther.*, 1922, **19**, 315—330).—Mercury salts produce in animals a sudden fall of blood-pressure and depression and paralysis of respiration, and in some cases profound cardiac disturbances. W. O. K.

Pharmacological Studies on Acetone. WILLIAM SALANT and NATHANIEL KLEITMAN (*J. Pharm. Expt. Ther.*, 1922, **19**, 293—306).—The pharmacological action of acetone is considerable, especially in inhibiting the respiration and heart-beat, and in producing fall of blood-pressure. It is particularly potent when a number of just active doses are given. W. O. K.

Toxicity of Scatole. WILLIAM SALANT and NATHANIEL KLEITMAN (*J. Pharm. Expt. Ther.*, 1922, **19**, 307—313).—Scatole is a toxic substance, causing depression of the circulation and of the central nervous system. W. O. K.

Chemistry of Vegetable Physiology and Agriculture.

Effect of Sugar on the Production of Indole. R. APPELMANS (*Compt. rend. Soc. Biol.*, 1921, **85**, 725—727; from *Chem. Zentr.*, 1922, i, 52—53).—The production of indole was studied in media with and without sugars; the sugars used being dextrose, maltose, sucrose, lactose, and mannitol. With *Bacillus coli* there is a general parallelism between the inhibition of indole production and gas formation; two exceptions were observed in the presence of sucrose. Similar results were obtained with *Proteus vulgaris*, *Bacillus pseudodysentericus*, cholera vibrio, and *Vibrio septicus*. The production of indole can occur when the fermentable material is used up. G. W. R.

Effect of Manganous Chloride on the Formation of Diphtheria Toxin. L. E. WALBUM (*Compt. rend. Soc. Biol.*, 1921, **85**, 619—620; from *Chem. Zentr.*, 1922, i, 51).—Diphtheria bacilli are cultivated in bouillon with 1.5% Witte peptone, 0.5% sodium chloride, and 0.2% invert-sugar. The formation of toxin is increased six-fold by the addition of 0.01 c.c. of *N*-manganous chloride to 1000 c.c. of the medium. Larger additions of manganous chloride decrease the formation of toxin. G. W. R.

Effect of Different Metallic Salts on the Formation of Staphylolysin. L. E. WALBUM (*Compt. rend. Soc. Biol.*, 1921, **85**, 376—377; from *Chem. Zentr.*, 1922, i, 51).—The addition of equivalent amounts of salts of magnesium, manganese, nickel, cadmium, gold, or platinum causes a decrease in the formation of staphylolysin; salts of other metals, particularly calcium, exert an inhibitory effect. G. W. R.

Nitrogen Nutrition of Yeast. FREDERICK K. SWOBODA (*J. Biol. Chem.*, 1922, **52**, 91—103).—The effect of various substances on the nitrogen nutrition of yeast was studied, the special feature of the experiments being the addition to the synthetic media employed of a constant quantity of growth-promoting vitamin ("bios"). In a medium containing asparagine, succinamide, succinimide, or aspartic acid, the growth is better in the presence than in the absence of ammonium sulphate. Of the nitrogen contained in asparagine, the α -amino-group appears to stimulate nitrogen assimilation; the amide-group, however, in the presence of ammonium sulphate, also stimulates cell reproduction. The nutrient value of edestin is increased by mild acid hydrolysis, but is decreased by continued acid hydrolysis and by alkaline hydrolysis. In the latter case, subsequent acid hydrolysis again improves its nutrient value. The effect of various amino-acids both in the presence and absence of hydrolysed edestin was also studied. E. S.

The Conditions Influencing the Formation of Fat by the Yeast-cell. IDA SMEDLEY MACLEAN (*Biochem. J.*, 1922, **16**, 370—379).—Ether extracts considerably more fat from yeast if the latter is first boiled with *N*-hydrochloric acid for two hours. This is because a large part of the fat is in some form of combination in the plasma of the cell. Yeast grown under unfavourable conditions shows a large increase in the fat content (up to 9%). Aeration, and a non-nitrogenous medium rich in carbohydrate result likewise in increased fat-content, the increase being in the combined fat. W. O. K.

The Capacity of Yeast to Degrade Acid Amides. WALTER DIETER (*Z. physiol. Chem.*, 1922, **120**, 281—291).—Sterile experiments with a top fermentation pure culture yeast show that it

does not remove the amide nitrogen from asparagine and other acid amides under conditions such that it ferments but does not grow. S. S. Z.

The Destruction of Lactic Acid by Yeast-cells. FRITZ LIEBEN (*Oesterr. Chem. Zeit.*, 1922, 25, 87—90).—Lactic acid is one of the products of the degradation of carbohydrates in muscle, and experiments were made *in vitro* to determine the ultimate fate of this substance under the influence of the ferments of the yeast-cell, which appear to be similar, at least, to the muscle enzymes. It was found that the lactic acid disappeared to within 3—5% in seven to eight hours under suitable conditions, and that about two-thirds of its carbon content appeared in the products as carbon dioxide, either liberated, or remaining combined with sodium; the remainder of the carbon was represented by an increase in weight of the yeast substance, and if calculated as $C_6H_{10}O_5$, practically accounted, with the carbon dioxide, for the whole of the lactic acid which had disappeared. It appears therefore that both synthesis and degradation had occurred simultaneously. No degradation products other than carbon dioxide could be detected. Similar experiments were made with vegetable acids and with amino-acids; the former were not attacked, the latter were in part consumed by the yeast, but no degradation to carbon dioxide could be detected. G. F. M.

Influence of Substances obtained from Yeast-cells and Organs on the Time Course of the Fission of Substrates by Polypeptidases, Carbohydrases, and Esterases. EMIL ABDERHALDEN and ERNST WERTHEIMER (*Fermentforsch.*, 1922, 6, 1—26).—The substances obtained from yeast by extraction with alcohol or by autolysis accelerate the fission of dipeptides by pancreas extract; this action requires both the dialysed and non-dialysed portions of the yeast extract and is annulled by boiling the latter. Certain of the optones behave similarly. Neither animal charcoal, nor kaolin, nor kieselguhr, nor talc adsorbs the peptolytic enzyme from yeast maceration juice, but the charcoal greatly retards the hydrolysis of *dl*-leucylglycine probably by adsorbing the dipeptide. The action of sucrase is retarded by alcoholic yeast extract; the retarding agent is non-dialysable, the dialysate being without effect. Diastatic action is not appreciably influenced by yeast extract or by various optones, and yeast extracts made in different ways are without influence on the action of lipase. T. H. P.

Influence of Hydrogen-ion Concentration on the Action of the Amylase of *Aspergillus niger*. G. L. FUNKE (*Proc. K. Akad. Wetensch., Amsterdam*, 1922, 25, 6—8).—*Aspergillus niger* produces large quantities of amylase which diffuses into the surrounding nutritive medium; at the same time, the fungus produces acids which give the medium a high hydrogen-ion concentration.

This appears to have no unfavourable action on the behaviour of the amylase, and in consequence it is concluded that the optimum action of amylase could not be at the same hydrogen-ion concentration as that of the ptyalin, which works best in a neutral or faintly acid solution. To test this point, the rate of hydrolysis of starch by amylase in the presence of buffer solutions has been investigated, and it is shown that there is no optimum concentration of hydrogen-ions, but a region where the action is at a maximum which lies between $P_H=3.5$ and $P_H=5.5$. The results confirm Michaëlis's view (A., 1911, i, 1052; ii, 577) that enzymes are ampholytes, and on this basis the dissociation constants of the acid and base are determined as $k_a=6.3 \times 10^{-7}$ and $k_b=2.884 \times 10^{-12}$. Similar determinations with the amylase of malt yield a similar optimum region; the values being $k_b=5.76 \times 10^{-11}$ and $k_a=6.3 \times 10^{-7}$.

J. F. S.

Biological Signification of Alkaloids in Plants. G. CIAMICIAN and C. RAVENNA (*Biochem. therap. experim.*, 1922, 9, 3—29).—A summary of the work carried out by the authors on this subject since 1908.

T. H. P.

The Distribution of Anthocyanidins in the Coloured Organs of Plants. ST. JONESCO (*Compt. rend.*, 1922, 174, 1635—1637; cf. *ibid.*, 1921, 173, 168, 426).—The anthocyanidins, either as a coloured pigment or in the free state, do not exist in all coloured tissues which contain anthocyanin. They appear to be characteristic of pure red organs, whilst in the blue, violet, or reddish-purple organs there occurs, in their place, a very intense, yellow pigment, and the anthocyanidins are entirely absent. This is shown to be the case for the violet-red leaves of beetroot, the violet flowers of *Gladiolus* and *Cobaea scandens*, the reddish-purple flowers of *Canna* and of a cultured rose, and the blue flowers of *Centaurea cyanus*. This yellow pigment is not coloured red by warming with 20% hydrochloric acid.

W. G.

Saponin from *Agave lechuguilla*, Torrey. CARL O. JOHNS, LEWIS H. CHERNOFF, and ARNO VIEHOEVER (*J. Biol. Chem.*, 1922, 52, 335—347).—A saponin, $C_{27}H_{44}O_{12}$, occurs in the cell-sap of *Agave lechuguilla*. It has been isolated in the form of an almost white, amorphous substance by extracting the air-dried rootstocks with 95% alcohol. It possesses hæmolytic action and is toxic towards fishes. On partial hydrolysis it yields dextrose and an amorphous pro-sapogenin, the latter being further hydrolysed to galactose and a sapogenin, $C_{15}H_{24}O_8$, acicular crystals or prisms, m. p. 183.5°, which is identical with that obtained from the saponin of *Yucca filamentosa* (A., 1917, i, 191).

E. S.

Comparative Plant Chemistry. III. *Campanula rotundifolia*, L. FRIEDRICH SPRINGER (*Monatsh.*, 1922, 43, 13—20).—The stems and leaves of the plant were examined. The portion of the dried material soluble in light petroleum, including

fats, chlorophyll, phytosterol, lecithin, and resinic acids, amounted to 6.09%. The crude fats gave an acid number 78.1, saponification number 130.8, iodine number 88.0, unsaponifiable 48.3%. The free fatty acids had m. p. 60–70°, but were insufficient in quantity for further examination. The ether-soluble resins in the dried material amounted to 2.01% and the alcohol-soluble portion to 17.39%. From the alcohol extract was extracted with ether a substance which, after purification, including reduction with zinc and hydrochloric acid, had m. p. 214–215° and a composition and molecular weight corresponding with $C_{22}H_{40}O_2$. The substance is semi-crystalline, shows Liebermann's cholesterol reaction, and is dextrorotatory, $[\alpha] +37.7$ (mean). By oxidation with aqueous permanganate it gives a product, m. p. 232°, showing Liebermann's phytosterol reaction. There is a marked resemblance between the substance and Zellner's resin alcohol, polyporol, obtained from fungi (A., 1913, i, 573). The alcoholic extract of the plant contained a considerable amount of tannin, and when this had been precipitated with lead acetate, the filtrate contained invert-sugar in which laevulose predominated, indicating the presence of inulin. The water-soluble portion of the dried plant, 24.87%, contained a small amount of inulin. The insoluble portion contained 12.89% of pentosans and 35.5% of fibre; total ash 4.43%. The milky sap is probably responsible for the rather high resin content of the plant.

E. H. R.

The Fatty Acids of Colza Oil. E. RAYMOND (*Bull. Soc. chim.*, 1922, [iv], 31, 414–419).—In the mixture of fatty acids obtained from the saponification of a sample of Indian colza oil, the author has identified the following fatty acids: erucic, linoleic, or linolenic giving soluble bromides, palmitic, oleic, stearic, and small amounts of linoleic or linolenic giving insoluble bromides.

W. G.

Effect of Cocaine on the Growth of *Lupinus albus*. DAVID I. MACHT and MARGUERITE B. LIVINGSTON (*J. Gen. Physiol.*, 1922, 4, 573–584).—Experiments were made on the inhibiting effect of cocaine and its products of hydrolysis (ecgonine, methyl alcohol, and benzoic acid) on the growth of the young roots of *Lupinus albus*. The results show that cocaine and ecgonine are relatively very much less toxic to the plant than to animals, whilst sodium benzoate, which is practically non-toxic to animals, is highly toxic to the plant.

C. R. H.

Effect of Nitrogenous Fertilisers on the Alkaloid Content of Lupines. VOGEL and E. WEBER (*Z. Pflanz. Düng.*, 1922, [A], 1, 85–95).—The alkaloid content of blue and yellow lupines respectively varies according as the plants receive their nitrogen through the medium of nitrogen fixing bacteria in root nodules, or from nitrogenous fertilisers. Smaller contents of alkaloid were observed in the latter than in the former type of nitrogen nutrition. The effect of certain materials for artificial inoculation was examined.

"Azotogen" and "nitragin" gave satisfactory results. "Azonutrin" was less satisfactory, whilst "legumin" was quite ineffective. A method for the estimation of alkaloids in lupines is described (cf. Mach and Lederle, A., 1921, ii, 718). G. W. R.

Comparative Plant Chemistry. I. *Lythrum Salicaria*, L.
 JULIUS ZELLNER (*Monatsh.*, 1921, 42, 453—458).—The stems and leaves without the flowers were examined, and their composition showed nothing of special interest. The dried plant contained 3.69% soluble in light petroleum, 1.73% in ether, and 16.36% in 95% alcohol; phlobaphen 1.86%, tannin 5.65%, dextrose 4.55%, total water-soluble 31.27%, water-soluble mineral matter 5.18%, mucus 8.08% (giving mucic acid when oxidised with nitric acid), free acid 3.55% (estimated by titration), total nitrogen 2.15%, ash 7.62%. No alkaloids or glucosides were found. As characteristic of the plant may be mentioned tannin, giving a blue colour with iron, a carbohydrate of the pectin type and a relatively large proportion of calcium sulphate. In the petals, besides anthocyanin was found an amorphous polysaccharide containing dextrose or invert-sugar. E. H. R.

The Presence of Melampyritol and Aucubin in the Foliated Stems of *Melampyrum arvense*, L. MARC BRIDEL and (MILE) MARIE BRÄCKE (*J. Pharm. Chim.*, 1922, 25, 449—457; cf. A., 1921, i, 840; this vol., i, 209).—From the entire plant of *Melampyrum arvense* the authors have extracted the glucoside aucubin, and a hexahydric alcohol, melampyritol or dulcitol. In examining the amount of glucoside present at different stages of the plant's growth, more than 2% of the glucoside was found in the plant after it had completed its life-cycle, when the stems were devoid of leaves. W. G.

The Carbohydrate Content of Navy Beans. MARIETTA EICHELBARGER (*J. Amer. Chem. Soc.*, 1922, 44, 1407—1408).—The author directs attention to results obtained by herself in 1919 which are in fairly close accord with those of Peterson and Churchill (A., 1921, i, 643), for the composition of navy beans. W. G.

The Constituents of the Pollen Grain of *Pinus sylvestris*.
 ALEXANDER KIESEL (*Z. physiol. Chem.*, 1922, 120, 85—90).—The ripe pollen contains potassium >0.59%, calcium >0.12%, trace of guanine, adenine, 0.02%, little histidine, arginine 0.52%, choline 0.21%, little colamine, and sucrose. The unripe pollen yielded very little in the nuclein bases fraction, and traces of histidine, arginine, and choline. S. S. Z.

The Presence of a Glucoside in the Stems and Roots of *Sedum Telephium*, L. MARC BRIDEL (*Bull. Soc. Chim. Biol.*, 1922, 4, 242—250).—The stems and roots of *Sedum Telephium*, L., contain a glucoside which has been isolated in an amorphous form. It reduces Fehling's solution slightly, has $[\alpha]_D - 28.57^\circ$, and is hydrolysed by sulphuric acid to dextrose and a substance possessing

an odour similar to that of terpineol. When hydrolysed by emulsin, a rose-like odour is produced. From these facts it is suggested that the first product of hydrolysis is an olefinic terpene which, under the influence of acids, isomerises to a cyclic terpene.

E. S.

The Proteins of the Seed of the Tomato, *Solanum esculentum*. CARL O. JOHNS and CHARLES E. F. GERSDORFF (*J. Biol. Chem.*, 1922, **51**, 439—452).—The meal which remains after extracting ground tomato seeds with ether contains 37.28% of protein (nitrogen $\times 6.25$). By extraction with salt solution followed by fractional precipitation of the extract with ammonium sulphate, an α - and a β -globulin have been isolated. Analysis by Van Slyke's method gave the following values for the basic amino-acids: α -globulin—cystine 1.28, arginine 13.97, histidine 1.16, lysine 4.89%; β -globulin—cystine 1.14, arginine 10.65, histidine, 3.80, lysine 6.35%. Qualitative tests were obtained for tryptophan and tyrosine in each case. Albumin and glutelin are absent from the seed.

E. S.

Relationship between Precipitation, Adsorption, and Charge on the Particles with particular reference to the Hydroxyl Ions. SANTE EMIL MATTSO (Koll. Chem. Beihefte, 1922, **14**, 227—316).—Using suspensions of quartz, clay, and humified sphagnum peat with particles of various sizes, the author has investigated the precipitating power of calcium salts in the presence of various concentrations of hydroxyl ions. The adsorption and charge on the particles during the precipitation of soil constituents by calcium salts in the presence of hydroxyl ions has also been investigated. The results are considered in connexion with the fertilisation of arable land by calcium compounds. It is shown that the hydroxyl ions are strongly adsorbed by soil and effect a discharging of the particles; in the presence of cations which have a weak or only moderately strong discharging effect they increase the action, since they facilitate the adsorption of the discharging cations. Precipitation is not only occasioned by the fact that the charge is reduced, since relatively strongly charged particles can be made to precipitate if the number of adsorbed ions is very large. The adsorbed ions appear to act as connecting links between the particles, and this is visualised by assuming that the positive ion attaches itself to two negative particles and so brings them together. Hydroxyl ions are not, of themselves, injurious to soil, but their action depends on the nature of the predominant cation in the soil. The hydroxides and oxides of iron and aluminium are negatively charged in aqueous suspensions, and only become positively charged by the adsorption of positive ions during the preparation. The power of soil to adsorb hydroxyl ions influences the solubility of various compounds and explains the acidity of many kinds of soil.

J. F. S.

Organic Chemistry.

Composition of Paraffin Wax. II. FRANCIS FRANCIS, CYRIL MERCER WATKINS, and REGINALD WILFRED WALLINGTON (T., 1922, 121, 1529—1535).

Formation of Hydrocarbons from Carbon Monoxide and from Formates. M. G. LEVI (*Giorn. Chim. Ind. Appl.*, 1922, 4, 302).—Tropsch and Schellenberg's criticisms (*Brennstoff-Chemie*, Feb., 1922) of Vignon's statements concerning the formation of methane in the water-gas process (A., 1921, i, 217) are in agreement with the results of Levi and Piva (A., 1914, i, 480; 1916, ii, 325).
T. H. P.

Preparation of Ethylene by Reduction of Acetylene. JOSEPH-MARIE-ALPHONSE CHEVALIER and PAUL BOURCET (F.P. 526129; from *Chem. Zentr.*, 1922, ii, 142).—Purified acetylene is passed through a solution of chromous sulphate (obtained by electrolytic reduction of chrome alum) in the presence or absence of electrolytically prepared hydrogen. The acetylene is rapidly absorbed with formation of ethylene which can be purified by repeated passage through chromous sulphate solution.
G. W. R.

The Action of Sodammonium on Hydrocarbons. P. LEBEAU and M. PICON (*Compt. rend.*, 1922, 175, 223—225).—Sodammonium has no action on aliphatic hydrocarbons excepting on the true acetylenes, which are partly converted into sodium compounds and the remainder is reduced by the hydrogen thereby liberated. Benzene and its homologues are also unattacked except in so far as the side chain, if containing a CH group, reacts like an open chain acetylene, or if containing a double bond adjacent to the nucleus it undergoes reduction, for example, styrene is converted into ethylbenzene. Terpene, terpinolene, carvene, terebene, α -pinene, and menthene are not attacked. Polycyclic hydrocarbons react in various ways. Stilbene and anthracene give dihydro-derivatives, the two benzene nuclei in each case remaining intact. Hydrocarbons the nuclei of which have two atoms of carbon in common have one nucleus only reduced by sodammonium, naphthalene, phenanthrene, etc., giving tetrahydro-derivatives. Diphenyl and dimethylfluorene also give tetrahydro-derivatives. Certain hydrocarbons having an acidic methylene group, for example, fluorene and indene, give sodium derivatives. The mechanism of the reduction is apparently complex, although the result may be expressed by the equation (for example, with naphthalene) $\text{C}_{14}\text{H}_{10} + 2\text{NH}_3\text{Na} = \text{C}_{14}\text{H}_{12} + 2\text{NH}_2\text{Na}$. Sodamide does not separate at low temperatures, however, but a red solution is formed, miscible with ether, which probably contains a sodammonium derivative of the hydrocarbon; this decomposes above -10° into sodamide and the reduction product.
G. F. M.

The Mobility and Valency Demand of the Ethyl Group in the Pinacolin Transformation. BERTIL NYBERGH (*Ber.*, 1922, 55, [B], 1960—1966).—Previous investigations have led Meerwein (*A.*, 1919, i, 162) to the conclusion that the various alkyl groups exhibit little regularity in their mobility in the pinacolin transformation. An examination of the behaviour of *s*- and *as*-dimethyldiethylethylene glycols [$\gamma\delta$ -dimethylhexane- $\gamma\delta$ -diol and β -methyl- γ -ethylpentane- $\beta\gamma$ -diol] shows that both alkyl groups are immobile; the former substance, however, yields mainly γ -methyl- γ -ethylpentane- β -one, whereas the latter gives chiefly ethyl *tert*-amyl ketone. It follows therefore that the ethyl group is actually much more mobile than the methyl radicle; but, on the other hand, the valency demand of the ethyl group does not appear to be so much less than that of the methyl group as Meerwein has supposed. The position of the ethyl group in comparison with that of other aliphatic residues is no longer unique; Meerwein's view of the periodicity of the valency demand of aliphatic residues remains unaffected. *as*- and *s*-Dimethyldiethylethylene glycol are converted by concentrated sulphuric acid at -10° into a mixture of ethyl *tert*-amyl ketone, b. p. $150.5-152^\circ$, d_{20}^{20} 0.8298, and γ -methyl- γ -ethylpentane- β -one, b. p. $153.5-154^\circ$, d_4^{20} 0.8389, which are separated in the form of their semicarbazones, m. p. 98° and 168° , respectively. The constitution of γ -methyl- γ -ethylpentane- β -one is deduced from the observation that it is oxidised by bromine and sodium hydroxide solution to bromoform, acetic acid, α -methyl- α -ethyl-*n*-butyric acid, and a crystalline acid, m. p. 82° , which in all probability is α -hydroxy- β -methyl- β -ethylpentoic acid.

H. W.

$\alpha\beta'$ -Dichlorodiethyl Ether. V. GRIGNARD and A. C. PURDY (*Compt. rend.*, 1922, 175, 200—203).— $\alpha\beta'$ -Dichlorodiethyl ether was prepared by the condensation, at $0-10^\circ$, of ethylene chlorohydrin (1 mol.) and paracetaldehyde ($\frac{1}{2}$ mol.) by means of dry hydrogen chloride. After separating the aqueous layer which is formed, the dried product is rectified, and the ether, which is a colourless, fuming liquid, distils at $55-57^\circ/17$ mm. It is rapidly decomposed by water and also on distillation under ordinary pressures, and decomposes slowly on keeping. It has d_{20}^{20} 1.1823, and n_D^{20} 1.4497. A small amount of the corresponding acetal, $\beta'\beta''$ -dichlorodiethylacetal, $\text{CH}_3\text{CH}(\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl})_2$, is also produced in the above reaction, and it may be obtained in 36% yield by condensing acetaldehyde (1 mol.) with ethylene chlorohydrin (2 mols.). It is a colourless liquid, distilling with partial decomposition at $196-198^\circ$ under ordinary pressures, and at $106-108^\circ/17$ mm. It has d_{20}^{20} 1.1712, and n_D^{20} 1.4532. On treatment with phosphorus pentachloride, it is converted into a mixture of $\alpha\beta'$ -dichlorodiethyl ether and ethylene dichloride.

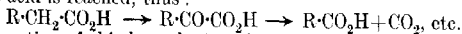
G. F. M.

Catalytic Decomposition of Formic Acid on Surfaces of Platinum and Silver. HAROLD CALVERT TINGEY and CYRIL NORMAN HINSELWOOD (*T.*, 1922, 121, 1668—1676).

The Catalytic Decomposition of the Lower Acids.
ALPHONSE MAILHE (*Bull. Soc. chim.*, 1922, [iv], **33**, 681—687; cf. A., 1909, i, 452).—The gaseous products obtained by heating acetic acid in the presence of copper-aluminium at about 600° are carbon monoxide, carbon dioxide, methane, and hydrogen. The same substances with the addition of other paraffins and of olefines are obtained from *isobutyric*, *butyric*, *isovaleric*, and *n-nonanoic* acids. There appears to be little relation between the acids and their decomposition products, except in the case of *isobutyric* and *isovaleric* acids. Equations are given showing the mechanism of formation of the products from the original material and the conclusion is drawn that ketones are formed as intermediate products. This is found to occur under the conditions of experiment and acetone, *isobutyron*e, *butyron*e, *isovaleron*e, and *nonylon*e have themselves been treated in a similar manner to the acids in order to verify the author's inferences. With increasing molecular weight of the acid, decomposition products of higher molecular weight are obtained; this is marked in the case of *n-nonanoic* acid which yields liquid unsaturated hydrocarbons. The latter, after hydrogenation, possess the properties of light petroleum. H. J. E.

The Oxidation of Potassium Acetate to Potassium Oxalate.
WILLIAM LLOYD EVANS and PAUL R. HINES (*J. Amer. Chem. Soc.*, 1922, **44**, 1543—1546).—Potassium acetate may be oxidised to potassium oxalate with alkaline permanganate under certain definite conditions. The yield of oxalic acid is a function of the concentration of the reacting materials, the temperature, and the duration of the experiment. H. W.

The Chromic Oxidation of the Homologues of Acetic Acid.
L. J. SIMON (*Compt. rend.*, 1922, **175**, 167—169).—Whilst within certain limits of temperature acetic acid is not attacked by a sulphuric acid-chromic acid mixture, it is completely converted into carbon dioxide by silver chromate under the same conditions. The homologues of acetic acid are likewise completely oxidised by silver chromate, but the chromic acid mixture leaves a non-combusted residue which for the homologues up to C_9 corresponds approximately with 1 atom of carbon, and increases slightly with the higher members, but never reaches 2. This result is interpreted by supposing that the acids are burnt atom by atom commencing with the carboxyl group, and the oxidation ceases when acetic acid is reached, thus:



Confirmation of this hypothesis is found in the oxidation of acetyl compounds and open-chain acids by lead chromate and sulphuric acid, where the evolution of gas accompanying the oxidation occurs in two well-defined stages, at a lower temperature corresponding with the more readily combustible part of the molecule, and at about 100°, the temperature at which acetic acid is oxidised by lead chromate. Methanesulphonic acid is not an intermediate product of chromic oxidation, as it is not oxidised even by silver chromate.

G. F. M.

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Synthesis of Fats (Glycerides). C. AMBERGER and K. BROMIG (*Biochem. Z.*, 1922, **130**, 252—266).—The use of a high temperature is inadmissible for the preparation of mixed glycerides of known constitution. Fischer and Pfähler's process (A., 1920, i, 807) has therefore been employed. α -Stearo- β -*dipalmitin*, m. p. 63.5°, occurs in goose fat, and was prepared from α -monostearin and palmityl chloride. β -Stearo- α -*dipalmitin*, m. p. 59.1°, was prepared from α -*dipalmitin*, m. p. 69.5°. The latter is prepared from β -*dipalmitin*- α -iodohydrin, m. p. 46.2°, by the action of silver nitrite. α -Palmito- β -*distearin*, m. p. 63.2°, was prepared from α -monopalmitin and stearyl chloride. The isomeric β -*palmito*- α -*distearin*, m. p. 67.9°, was prepared from α -*distearin*. α -Palmito- β -*diolein*, prepared from α -palmitin, was an oil. α -*Olein*, a pale yellow oil, yields α -oleo- β -*distearin*, m. p. 42°. H. K.

Acids of Montan Wax. H. TROPSCH and A. KREUTZER (*Brennstoff-Chemie*, 1922, **3**, 177—180, 193—198, 212—215).—The small quantity of humic acids contained in montan wax can be extracted by treatment of the lignite with benzene or a mixture of benzene and alcohol. In 1852, Brückner isolated, from the lignite of Gerstewitz, an acid (geocerinic acid), $C_{28}H_{56}O_2$, m. p. 82°. Hell obtained this acid, m. p. 83—84°, by saponification of the refined wax with potassium hydroxide, etc., and assigned to it the formula $C_{29}H_{58}O_2$. Montanic acid was first so named by von Boyen, in 1901. The raw wax on which the authors carried out their investigations had a melting point of 80°, an acid value of 34.1, and a saponification value of 82.8. It was saponified, and the dried soap extracted with benzene. The residue consisted of the potassium salts of the acids in the wax. After purification, the acid had m. p. 84° and an equivalent weight of 420.2. On treatment with permanganate, however, the greater part of the product separated out and gave an equivalent weight of 416.5 and m. p. 80°. The acid was esterified, and the product fractionated under reduced pressure. From the fraction, b. p. 265—267.5°, an acid, $C_{27}H_{54}O_2$, crystallising in bunches of needles, m. p. 82°, was obtained, and proved to be identical with an acid prepared from Chinese wax by Gascard (A., 1920, i, 470). This investigator showed that the acid which he had isolated was not identical with cerotic acid from beeswax. The authors give the name *carboceric acid* to the new compound. From the fraction of esters boiling between 260° and 275° small quantities of an acid, $C_{25}H_{50}O_2$, m. p. 78°, were obtained, which is seemingly identical with the hyenic acid isolated by Carius from the fat of certain glands of the hyæna. True montanic acid was isolated, and the formula $C_{29}H_{58}O_2$ confirmed. It crystallises in needles very similar to fir-tree branches, and has m. p. 86.5°. A. G.

Synthesis of Δ^8 -Decenoic Acid. AD. GRÜN and TH. WIRTH (*Ber.*, 1922, **55**, [B], 2206—2218).—The synthesis of Δ^8 -decenoic acid from undecylenic acid and from suberic acid is recorded. The

substance is identical with the acid isolated by Grün and Wirth (following abstract) from butter fat.

Ethyl undecenoate is reduced by sodium and ethyl alcohol to *undecenol*, $\text{CH}_2\text{CH}(\text{CH}_2)_8\text{CH}_2\text{OH}$, b. p. $250^\circ/\text{atmospheric pressure}$, $122^\circ/3 \text{ mm.}$, m. p. -7° , which is converted by chlorosulphonic acid in dry ethereal solution into *undecenyl hydrogen sulphate* (the barium salt, colourless leaflets, is described). Oxidation of the ester (or of the corresponding acetate) with chromic acid or preferably with permanganate leads to the isolation of *α -hydroxydecoic acid*, $\text{OH}\cdot\text{CH}_2(\text{CH}_2)_8\text{CO}_2\text{H}$, indistinct, transparent crystals, m. p. 75° (methyl ester, m. p. 34.5° , b. p. $154^\circ/7 \text{ mm.}$, amyl ester, b. p. $179\text{--}180^\circ/8 \text{ mm.}$). *α -Acetoxydecoic acid* has b. p. $213^\circ/15 \text{ mm.}$; at $320^\circ/\text{atmospheric pressure}$ it loses acetic acid, but the formation of the olefinic acid proceeds only slowly. *Methyl α -acetoxydecoate* is a moderately mobile liquid, b. p. $175^\circ/17 \text{ mm.}$, $295\text{--}300^\circ/\text{atmospheric pressure}$. *Amyl α -acetoxydecoate*, b. p. $210^\circ/15 \text{ mm.}$, $310\text{--}312^\circ/\text{atmospheric pressure}$ (when rapidly distilled), decomposes more readily than the methyl ester into the unsaturated compound when it is heated. The derivatives just described are too stable to permit a ready transition from hydroxydecoic to decenoic acid, but better results are obtained after the introduction of a heavier radicle. Thus, *methyl α -stearoxydecoate*, colourless, wax-like aggregates, m. p. 43° , decomposes readily when distilled under atmospheric pressure into stearic acid and methyl decenoate; the latter on hydrolysis gives decenoic acid, b. p. $143^\circ/6 \text{ mm.}$, whereas the product from butter fat has b. p. $142^\circ/4 \text{ mm.}$

Methyl α -chlorodecoate, b. p. $153^\circ/15 \text{ mm.}$, could not be converted satisfactorily into methyl decenoate by loss of hydrogen chloride.

The preparation of alkyl hydrogen sebacates by partial esterification of sebacic acid cannot be satisfactorily accomplished, and the acid esters are obtained by partial hydrolysis of the normal compounds. Methyl sebacate crystallises in long, transparent prisms, m. p. $27\text{--}28^\circ$ (literature, m. p. 36° and 38°), whereas the ethyl ester is a liquid, b. p. $172^\circ/7 \text{ mm.}$ *Ethyl hydrogen sebacate* forms colourless, indistinct crystals, m. p. 36° , b. p. $210^\circ/18 \text{ mm.}$; when distilled under atmospheric pressure it is decomposed into sebacic acid and ethyl sebacate. Potassium ethyl sebacate is reduced by sodium and boiling ethyl alcohol to *α -hydroxydecoic acid*.

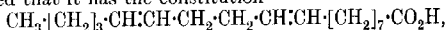
The iodine and acid numbers of Δ^9 -decenoic acid gradually diminish when the substance is preserved, thus indicating the formation of a lactone. Decenoic acid is converted by sulphuric acid (80%) at 90° into *decalactone*, $\text{C}_{10}\text{H}_{18}\text{O}_2$, a liquid, b. p. $153^\circ/15 \text{ mm.}$, which is saturated and neutral in character. It is hydrolysed by alcoholic potassium hydroxide solution with the production of a hydroxy-acid, leaflets, m. p. 44° , which gradually passes when preserved into water and the lactone. In all probability the substances are γ -decalactone and γ -hydroxydecoic acid, but this is not regarded as established definitely. H. W.

Δ^6 -Decenoic Acid, a Previously Unknown Acid from Butter.

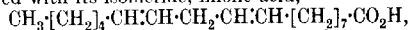
AD. GRÜN and TH. WIRTH (*Ber.*, 1922, 55, [B], 2197—2205).—Butter fat is treated with methyl-alcoholic hydrogen chloride (1.5%) and the methyl esters are submitted to fractional distillation whereby a portion, b. p. 100—140°/15 mm., iodine number 9.8, is obtained. The fraction is hydrolysed and a partial separation of the saturated and unsaturated acids is effected by systematic treatment of the corresponding lead salts in the usual manner. A mixture of approximately equal amounts of decenoic and decolic acids is thus produced which cannot be more completely separated by any of the ordinary methods. It is therefore esterified and the methyl esters are brominated in dry chloroform solution. The products are readily separated from one another by distillation under diminished pressure, whereby *methyl dibromodecoate*, b. p. 185—186°/7 mm., is obtained. Treatment of the latter with 5*N*-methyl alcoholic hydrogen chloride and zinc yields *methyl Δ^6 -decenoate*, a colourless, mobile liquid, b. p. 115—116°/12 mm., which is hydrolysed to *Δ^6 -decenoic acid*, $\text{CH}_3\cdot\text{CH}[\text{CH}_2]_7\cdot\text{CO}_2\text{H}$, a colourless, fairly mobile liquid, b. p. 142°/4 mm., m. p. below 0°. The constitution of the acid is deduced from its conversion by ozone into azelaic and formic acids. This is the first instance on record of the isolation of an unsaturated acid of such low molecular weight or of one containing a terminal unsaturated bond, from a natural fat.

H. W.

China Wood Oil. K. H. BAUER and K. HERBERTS (*Chem. Umschau*, 1922, 29, 229—232).—China wood oil occupies a special position among the drying oils in containing practically no saturated acid and very little oleic acid, elaeostearic acid, $\text{C}_{18}\text{H}_{32}\text{O}_2$, having two unsaturated double bonds, being the characteristic acid. This acid, which forms large, colourless crystals, m. p. 48°, is designated α -elaostearic acid, whilst the β -form, to which it easily changes spontaneously, has m. p. 71°. Such transformation also takes place with the glyceride by exposure to light, or the catalytic influence of iodine, sulphur, etc. Since α -elaostearic acid on hydrogenation yields stearic acid, it is considered to be a straight chain fatty acid of the C_{18} series. From examination of the decomposition products of the ozonide of α -elaostearic acid, and from the results of oxidation by potassium permanganate, it is concluded that it has the constitution



as compared with its isomeride, linolic acid,



the melting points of the tetrabromides from these two acids being 114° and 114.5°, respectively. Nicolet has proved their separate identity by the considerable lowering of melting point which occurs when the two are mixed. This has been confirmed by the authors, who debrominated the bromo-derivative of α -elaostearic acid by means of zinc dust in alcohol and obtained a product free from bromine having m. p. 68—70°, β -elaostearic acid having m. p. 71°, thus showing a transformation of the α -form into the β -form and

a distinction of the bromo-derivatives of both forms from that of linolic acid. By esterification of α -elæostearic acid with methyl alcohol in the presence of sulphuric acid, separation of the ester by distillation (b. p. $220^{\circ}/35$ mm.) and subsequent saponification and separation of the acid, β -elæostearic acid alone, m. p. $69-70.5^{\circ}$, was found, the change from the α - to the β -form being attributed, not to the action of the alkali used for saponification, but to the sulphuric acid used in esterification, a result somewhat comparable with the observed obtainment of the β -glyceride by mere extraction of the seed with carbon disulphide. By saponifying the anhydride obtained by heating α -elæostearic acid with acetic anhydride and liberating the free acid, the original α -elæostearic acid was obtained with m. p. 46° . The authors conclude that the transformation of α -elæostearic acid into its β -isomeric form is most probably not accounted for by the mere action of light, since exposure to light was as far as possible avoided and conditions maintained as equal as possible in the two experiments of esterification of α -elæostearic acid and saponification of its anhydride respectively.

A. DE W.

The Colouring Constituents of Montan Wax. J. MARCUSSEN and H. SMELKUS (*Chem. Ztg.*, 1922, **46**, 701-702).—On extracting montan wax with ether in a Soxhlet apparatus, 23% of the wax dissolves and the solution, on being mixed with an equal volume of 96% alcohol and cooled to -20° , yields 18% of low-melting wax which contains about 6% of hydroxy-acids. The ether-alcohol solution contains 9% of a resin having a dark brown colour and dissolving readily in benzene, chloroform, and pyridine. On heating with sulphuric acid the resin yields a green, insoluble compound containing 4% of sulphur; with fuming sulphuric acid a black mass containing 7.8% of sulphur and slowly soluble in water is formed, whilst nitric acid gives a characteristic cyclic nitro-compound.

The residue of the original wax insoluble in ether contains about 10% of a brownish-black, unsaponifiable substance soluble in benzene, whilst the remainder consists of esters of a mixture of hydroxy-acids. These acids form a dark brown, friable mass, which contains 3.1% of sulphur, is soluble in benzene, chloroform, and amyl alcohol, has a saponification value of 94, acid value 58, iodine value 13, and on reduction with sodium in amyl alcohol solution yields a mixture of fatty acids. No humic acids could be detected in the mixture. The potassium salts are soluble in 50% alcohol, benzene, and hot water.

A. R. P.

Some Derivatives of Ethyl Hydrogen Diethylmalonate. PHILIPPE DUMESNIL (*Bull. Soc. chim.*, 1922, [iv], **33**, 687-689; cf. A., 1921, i, 391).—The following substances have been prepared from ethyl hydrogen diethylmalonate. *Ethyl diethylmalonyl chloride*, $\text{COCl}\cdot\text{CEt}_2\cdot\text{CO}_2\text{Et}$, a colourless mobile liquid, b. p. $102^{\circ}/20$ mm., which gives the usual reactions of acid chlorides. *Ethyl diethylmalonic anhydride*, $\text{O}(\text{CO}\cdot\text{CEt}_2\cdot\text{CO}_2\text{Et})_2$, a colourless liquid, b. p. $210^{\circ}/24$ mm., which reacts with ammonia, yielding the corre-

sponding amide; attempts at esterification were unsuccessful. Ethyl diethylmalonamide (cf. Conrad and Zart, A., 1905, i, 754), formed by the action of ammonia on both the acid chloride and the anhydride; the *diethylamide*, $\text{NEt}_3 \cdot \text{CO} \cdot \text{C}(\text{Et})_2 \cdot \text{CO}_2 \cdot \text{Et}$, a colourless liquid, b. p. $170^\circ/28$ mm., by the action of diethylamine on the acid chloride; *benzyl ethyl diethylmalonate*, from the acid chloride and benzyl alcohol, a colourless liquid, b. p. $187^\circ/22$ mm. H. J. E.

Some Derivatives of *n*-Butylmalonic Acid. ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1922, **44**, 1578—1581).—A number of new derivatives have been prepared from ethyl *n*-butylmalonate. Of chief interest among these is 5-ethyl-5-*n*-butylbarbituric acid, which is a powerful hypnotic. The substitution of a phenoxy-group for either of the alkyl radicles in this substance destroys its physiological activity.

Ethyl *n*-butylmalonate is converted by concentrated aqueous ammonia into *n*-butylmalonamide, slender, hair-like needles, m. p. 200° , and by aqueous methylamine (33%) into *n*-butyl- NN' -dimethylmalonamide, colourless, glistening needles, m. p. 184° . *n*-Butylmalonanilide, colourless needles, m. p. 193° , is prepared by heating a mixture of aniline and ethyl *n*-butylmalonate at its boiling point; the similarly prepared *n*-butylmalono-*o*-toluidide crystallises in colourless needles, m. p. 202° . 5-*n*-Butylbarbituric acid, m. p. 214° , is converted by bromine in methylalcoholic solution into 5-bromo-5-*n*-butylbarbituric acid, colourless needles, m. p. 114° . Ethyl bromo-*n*-butylmalonate, a colourless liquid, b. p. $152\text{--}153^\circ/20$ mm., $252\text{--}253^\circ$ (decomp.)/737 mm., d_4^{25} 1.238, is obtained by the addition of bromine, containing a trace of iodine as catalyst, to ethyl *n*-butylmalonate; it is transformed by an alcoholic solution of sodium phenoxide into ethyl phenoxy-*n*-butylmalonate, a viscous liquid, b. p. $170\text{--}173^\circ/8$ mm., d_4^{25} 1.063. The latter ester is converted by carbamide and ethyl alcoholic sodium ethoxide solution at 105° into 5-phenoxy-5-*n*-butylbarbituric acid, small, colourless needles, m. p. 167° . Ethyl ethylbutylmalonate, b. p. $243\text{--}245^\circ/755$ mm., is converted in a similar manner into 5-ethyl-5-*n*-butylbarbituric acid, m. p. 125° .

H. W.

Action of α -Bromoisobutaldehyde on Sodiomalonic Ester. ADOLF FRANKE and GERALD GROEGER (*Monatsh.*, 1922, **43**, 56—60).—The reaction between ethyl sodiomalonate and α -bromoisobutaldehyde takes an unexpected course, yielding the ethyl ester of γ -isobutylidenemalonolactone, transparent crystals, m. p. 68° ; b. p. $177\text{--}178^\circ/25$ mm., which, on oxidation by cold alkaline permanganate, gives $\alpha\beta$ -dihydroxy- γ -isohexolactone, m. p. 97° . Condensation of the same aldehyde with ethyl sodioacetoacetate gives a substance, $\text{C}_{10}\text{H}_{16}\text{O}_4$, b. p. $135\text{--}140^\circ$. C. K. I.

A New Class of Active Racemic Substances. PH. LANDRIEU (*Bull. chim.*, 1922, **33**, 667—672; cf. Délépine, A., 1921 ii, 567).—A compound of *d*-tartaric acid with inactive tartari

acid was prepared, containing one molecule of each acid with two molecules of water of crystallisation, the rotatory power of which is equal to half that of the active acid. In order to prove that the substance was a compound and not a mixture, its equilibrium with the mother-liquor from which it was crystallised was studied at a temperature of 13.5° , and the conditions under which either of the acids or the compound of the two could be deposited were ascertained. The equilibrium diagram is given and a similar curve was obtained from *L*-tartaric acid and the inactive form. The conclusion is drawn that it should be possible to obtain a triple compound of these acids which should be regarded as a compound of racemic acid with the inactive form. The author considers that, in order to obtain molecular compounds of optically active substances, it is not necessary that the activity of those substances should be of opposite sign.

H. J. E.

Preparation of Methyleneitic Acid. C. GASTALDI (*Boll. Chim. Farm.*, 1922, **61**, 353—357).—When 40 grams of crystallised citric acid and 6 grams of paraformaldehyde are heated together at 145° in a sealed tube of 90 c.c. capacity, methyleneitic acid is formed in 74% yield.

T. H. P.

Synthesis of the Polyacetic Acids of Methane. VII. *iso*Butylene- $\alpha\gamma\gamma'$ -tricarboxylic Acid and Methanetetra-acetic Acid. CHRISTOPHER KELK INGOLD and LEWIS CHARLES NICKOLLS (*T.*, 1922, **121**, 1638—1648).

Methylated Saccharic Acid and Methylated Mucic Acid. P. KARRER and J. PEYER (*Helv. Chim. Acta*, 1922, **5**, 577—581).—Potassium saccharate was methylated first with methyl sulphate in alkaline solution, and when the partly methylated product had been freed from inorganic salts, methylation was completed by boiling with methyl iodide in presence of silver oxide. Purified *methyl tetramethylsaccharate*, $\text{CO}_2\text{Me}[\text{CH}(\text{OMe})_2]_4\text{CO}_2\text{Me}$, crystallises from ether in stout needles or plates, m. p. 68° , $[\alpha]_D^{25} +8.88^{\circ}$ to 10.26° . *Tetramethylsuccharodiamide*, prepared by the action of ammonia on a cold concentrated aqueous solution on the above compound, forms colourless, apparently rhombic plates, m. p. 237° ; $[\alpha]_D^{25} -12.22^{\circ}$ in water. Mucic acid, when methylated in a similar manner to saccharic acid, gives *methyl tetramethylmucate*, crystallising in monoclinic or rhombic tablets, m. p. 103° . A second product, isolated in small quantity, is probably *methyl trimethylmucate*, m. p. $165-166^{\circ}$. *Tetramethylmucodiamide* forms small, tabular crystals, m. p. 276° . *Barium tetramethylsaccharate* crystallises in long needles, very soluble in water; the silver salt forms a very soluble, white powder.

E. H. R.

The Alcoholic Fermentation of Formaldehyde. HANS MÜLLER (*Helv. Chim. Acta*, 1922, **5**, 627—628).—To account for the alcoholic fermentation of formaldehyde by osmium, E. Müller supposed the intermediate formation of a compound, H_2CO_2 , containing sexavalent carbon (this vol., i, 114). On account of the widespread nature of Cannizzaro's reaction in physiological

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change, it is interesting that in this case also it will explain the observed facts. Assuming that 2 mols. of formaldehyde give 1 mol. of methyl alcohol and 1 mol. of formic acid, the last can also behave as an aldehyde and by the same reaction give 0.5 mol. of formaldehyde and 0.5 mol. of carbon dioxide. The formaldehyde thus regenerated starts the cycle again. The products of fermentation, methyl alcohol and carbon dioxide, are thus produced in the molecular ratio 2 : 1, in agreement with the experimental results. E. H. R.

Asymmetric Synthesis. J. PIRAK (*Biochem. Z.*, 1922, **130**, 76—79).—The combination of sodium hydrogen sulphite and acetaldehyde and subsequent addition of potassium cyanide was carried out slowly in the circularly polarised light from a metal filament lamp of 250 candle power or from a mercury lamp. The cyanohydrin was converted into lactic acid. The latter was invariably inactive, even in presence of molybdic acid. H. K.

The Preparation of Aldehydes from Tertiary Alcohols. R. LOCQUIN and SUNG WOUSENG (*Compt. rend.*, 1922, **175**, 100—102).—It has previously been shown (this vol., i, 710) that tertiary alcohols of the type $\text{HO}\cdot\text{CRR}'\cdot\text{CH}\cdot\text{CH}_2$ are readily converted by acids into primary alcohols of the type $\text{CRR}'\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$, and it is now shown that, if these tertiary alcohols are acted on by chromic acid mixture, they give aldehydes of the type $\text{CRR}'\cdot\text{CH}\cdot\text{CHO}$.

Thus this oxidation process is not necessarily a means of differentiating a primary from a tertiary alcohol. W. G.

Preparation of Ketones from Secondary Alcohols. SETH BLISS HUNT (F.P. 523108; from *Chem. Zentr.*, 1922, ii, 142).—Secondary alcohols in the state of vapour are mixed with oxygen and an indifferent gas in the presence of metallic catalysts, preferably copper or copper alloys, at 475—800°. Acetone is thus prepared from an alcoholic mixture containing principally isopropyl alcohol (from petroleum hydrocarbons). The alcohol, heated at 65°, is mixed with sufficient air for its oxidation and the mixture is passed over a copper catalyst at 500°. The yield of acetone amounts to 75% of the theoretical yield. G. W. R.

Catalysis. XVI. The Inversion of Sucrose by Hydrogen Ion. THOMAS MORAN and WILLIAM CUDMORE McCULLAGH LEWIS (T., 1922, **121**, 1613—1623).

Methyl Ethers of Xylan. EMIL HEUSER and WILHELM RUPPEL (*Ber.*, 1922, **55**, [B], 2084—2088; cf. Heuser, Braden, and Kürschner [this vol., i, 113]).—The presence of two hydroxyl groups in xylan has been shown by the formation of a diacetate and dibenzoate, and is now further confirmed by the production of a dimethyl ether.

Although xylan is very readily soluble in solutions of alkali hydroxides, it cannot be converted by methyl sulphate in these media into methylated products containing more than 1—1.5

methoxyl groups for each $C_5H_8O_4$ complex. The products thus obtained are freely soluble in cold water, but the solutions become turbid when they are warmed owing to separation of methyloxylan. Better results are obtained with silver oxide and methyl iodide. Xylan, pre-methylated with sodium hydroxide and methyl sulphate, is almost completely methylated by these reagents boiling under slightly increased pressure, and is completely converted into *dimethylxylan*, a brittle mass which softens at $65-70^\circ$, when similarly treated under pressure at 100° .
H. W.

Constitution of Polysaccharides. I. Xylan and its Acetyl Derivatives. I. SHIGERU KOMATSU and KOZO KASHIMA (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1922, 5, 307-314).—The isolation of xylan from wheat straw and corn cobs is described in detail. It is noteworthy that xylan prepared from the latter source yields scarcely any acetyl derivative by the action of acetic anhydride and acetyl chloride with or without catalytic agents, whereas that derived from wheat straw easily yields acetyl compounds.

Monoacetylxylan, $[\alpha]_D^{20} -202^\circ 6'$ when dissolved in chloroform (cf. Bader, T., 1896, 70, 1335), is prepared from xylan and acetyl chloride, or in better yield from xylan, and glacial acetic acid and acetic anhydride containing chlorine and sulphur dioxide. Its molecular weight in boiling chloroform solution corresponds with the formula $(C_7H_{10}O_5)_2$. Diacetylxylan (cf. Bader, *loc. cit.*) is prepared by treating xylan with acetyl chloride and pyridine, acetic anhydride, chlorine, and sulphur dioxide, or acetic anhydride and zinc chloride; it has $[\alpha]_D^{20} -135^\circ 9'$ in chloroform solution.

The hydrolysis of xylan and its acetates by *N*/5-benzenesulphonic acid has been investigated.
H. W.

Galactosan. AMÉ PICTET and HENRY VERNET (*Helv. Chim. Acta*, 1922, 5, 444-448).—Galactosan is difficult to separate from its polymerisation products. When galactose is dehydrated at $180^\circ/15$ mm., the molecular weight of the product corresponds with $(C_5H_{10}O_5)_3$; at $145^\circ/15$ mm. the product corresponds with $(C_6H_{10}O_5)_2$, whilst at $135^\circ/2$ mm. the product, which is very hygroscopic, appears to be a mixture of galactosan and digalactosan. The galactosan was partly purified by extraction with boiling alcohol, in which it is more soluble than its polymerides. In its chemical behaviour it is similar to glucosan, and is undoubtedly an anhydride of the α -series. It polymerises slowly at the ordinary temperature; in the hot, polymerisation is accelerated by zinc chloride, which brings about, at 170° , the formation of a mixture of tetra- and penta-galactosan.

With cold hydrochloric acid, galactosan forms galactosyl chloride, but the product is contaminated with polygalactosides, through the polymerising action of the acid. The impure α -galactosyl chloride forms a transparent, brown, amorphous residue from alcohol. Condensed with dextrose and sodium in alcoholic solution, it forms a disaccharide, probably *glucose- α -galactoside*, giving an *osazone*, yellow needles, m. p. 158° . This *osazone* is not identical

with that of glucose- β -galactoside prepared by Fischer and Armstrong (A., 1902, i, 746). E. H. R.

Sublimation Experiments with Carbohydrates. P. KARRER and J. O. ROSENBERG (*Helv. Chim. Acta*, 1922, 5, 575—576).—It was shown by Pictet and Sarasin (A., 1918, i, 59) that when starch was distilled under reduced pressure, levoglucosan could be identified in the distillate. The same compound has now been obtained as a sublimate by heating potato starch at about 220° in a very thin layer, having a cold condensing surface within 2 mm. of the heated starch, at atmospheric pressure. Levoglucosan was obtained in a similar manner from α -tetra-amylose at 220°, and with rhamnose at 120°/12 mm. the sugar itself was sublimed. E. H. R.

Viscosity of Cellulose in Cuprammonium Hydroxide Solution. I. Determination of the Viscosity. REGINALD ARTHUR JOYNER (T., 1922, 121, 1511—1525).

Constitution of Polysaccharides. V. The Yield of Glucose from Cotton Cellulose. JAMES COLQUHOUN IRVINE and EDMUND LANGLEY HIRST (T., 1922, 121, 1585—1591).

Oxidation of Lignin and Lignosulphonic Methyl Ethers. EMIL HEUSER and SIGURD SAMUELSEN (*Cellulosechem.*, 1922, 3, 78—83).—Hitherto it has not been possible, by the oxidation of lignin or lignosulphonic acid, to obtain products intermediate between the original complex and oxalic acid. It was thought, by analogy, that the complete methoxylation of the lignin might stabilise the molecule and lead to oxidation products having a direct constitutional relationship to the original lignin. Both lignosulphonic acid and lignin isolated by Willstätter and Zechmeister's method were completely methoxylated by six successive treatments with methyl sulphate and sodium hydroxide at 70°. The methoxyl value of the sulphonic acid was thus increased from 13.07 to 25.43% and that of the lignin from 14.15 to 26.05%. These products were then oxidised by alkaline permanganate at 90° and by alkaline peroxide, but no product other than oxalic acid could be isolated. The volatile acids, calculated as acetic, amounted only to 0.9% of the methyl-lignin oxidised. A statistical account of the oxidation of methyl-lignin by alkaline permanganate showed 44.76% of the original carbon in the form of carbon dioxide and 10.69% in the form of oxalic acid; thus only 55.55% of the total carbon oxidised has been accounted for. J. F. B.

The Effect of Dakin's Hypochlorite Solution on certain Organic Substances. N. O. ENGELDT (*Z. physiol. Chem.*, 1922, 121, 18—61).—The action of Dakin's hypochlorite solution, containing 0.5% of sodium hypochlorite, 0.5% of sodium carbonate, and 0.45% of sodium hydrogen carbonate, on carbohydrates, fats, soaps, and glycerol, proteins, amino-acids, ammonia, and aldehydes, has been investigated. The general method is to treat a given amount of the substance with the hypochlorite solution for a given time at a given temperature, and to estimate the amount of hypo-

chlorite left by treatment with an iodide and estimation of the iodine set free. Fats, soaps, and glycerol react only to a small extent; most of the other substances investigated react much more completely and rapidly. In particular, hippuric acid is found to be attacked, yielding benzoic acid, formaldehyde, and ammonia, in opposition to the results of Langheld (A., 1909, i, 138, 557) and Dakin. W. O. K.

Optically Active Amine Oxides. III. JAKOB MEISENHEIMER (*Annalen*, 1922, **428**, 252—253).—A general introduction to the accompanying papers (cf. following abstracts, and this vol., i, 822). C. K. I.

Optically Active Amine Oxides. III (i). Methylethylpropylamine Oxide. J. MEISENHEIMER and HERMANN BERNHARD (*Annalen*, 1922, **428**, 254—268).—The optical resolution of this oxide was not accomplished although the *d*-bromocamphorsulphonate, *d*-tartrate, and *d*-camphornitronate were fractionally crystallised.

Methylethylpropylamine, prepared from propyl bromide and methylethylamine, has b. p. 91—92°, yields a *hydrochloride*, m. p. 177—179°, a *picrate*, m. p. 94—95°, and a *platinichloride*, m. p. 176—177°. The oxide is extremely hygroscopic, and yields a *hydrochloride*, m. p. 53—56°, a *picrate*, m. p. 106—107°, a *platinichloride*, m. p. 204—216°, a *d*-bromocamphorsulphonate, m. p. 89—91°, a *d*-tartrate, m. p. 99—100°, and a *d*-camphornitronate, m. p. 82—83°. C. K. I.

Optically Active Amine Oxides. III (ii). Methylethylallylamine Oxide. J. MEISENHEIMER and ARTUR LOHSNER (*Annalen*, 1922, **428**, 269—278).—Methylethylallylamine oxide has been resolved into its optical antipodes by fractional crystallisation of its *d*-bromocamphorsulphonate.

Methylethylallylamine, prepared from methylethylamine and allyl bromide, has b. p. 88—89°, forms a *picrate*, m. p. 90°, and an *oxide*, which gave a *dl*-*picrate*, m. p. 134—135°. The *d*-bromocamphorsulphonate of the *l*-amine oxide, which was crystallised from ethyl acetate, crystallises with 1H₂O, has m. p. 66—68°, and yields the *l*-*picrate*, having m. p. 133—134° and $[\alpha]_D -2.6^\circ$. The *d*-bromocamphorsulphonate of the *d*-amine oxide, which was purified with the aid of ethyl nitrate, crystallises with 2H₂O, has m. p. 57—58°, and gives the *d*-*picrate*, m. p. 133—134°, $[\alpha]_D +2.9^\circ$. C. K. I.

Proteinogenous Amino-alcohols and Cholines. II. P. KARRER, M. GISLER, E. HORLACHER, F. LOCHER, W. MÄDER, and H. THOMANN (*Helv. Chim. Acta*, 1922, **5**, 469—480).—In a previous paper (A., 1921, i, 228) the preparation was described of a number of amino-alcohols and cholines from naturally occurring amino-acids. On account of their close crystallographic, chemical, and physiological relation to one another and their possible occurrence in the plant and animal organism, the study of these compounds has been extended. In most cases the racemic forms only were prepared.

Alanine-choline was prepared in the following stages. α -Bromopropionic acid was condensed with dimethylamine, and the crude product esterified with ethyl alcohol, giving *ethyl α -dimethylamino-propionate* (*N*-dimethylalanine ethyl ester), a pale yellow oil, b. p. $150^{\circ}/740$ mm. This was reduced with sodium and alcohol, giving *N*-dimethylalaninol, a pale yellow oil, b. p. $140-141^{\circ}/738$ mm. With methyl iodide, this readily gives *alanine-choline iodide*, $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{NMe}_3\text{I}$, m. p. 296° . Free *alanine-choline* is similar to the base of ordinary choline and very hygroscopic. Its *aurichloride*, $\text{C}_6\text{H}_{16}\text{ON}\cdot\text{AuCl}_4$, has m. p. 247° . The *platinichloride*, $(\text{C}_6\text{H}_{16}\text{ON})_2\text{PtCl}_6$, m. p. 228° , crystallises in stout, rhombic prisms, $a:b:c=0.7072:1:0.5689$; $d^{20} 1.863$. The *picrate* of alanine-choline forms golden-yellow crystals, m. p. 265° .

Valinol, $\text{CHMe}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{OH}$, was prepared by the reduction of valine ethyl ester (ethyl α -aminoisovalerate); it forms a colourless oil with a strong odour, b. p. $181-186^{\circ}/720$ mm.; the *hydrochloride*, m. p. 114° , is very hygroscopic. Valine-choline was synthesised as follows: α -Bromoisovaleric acid was condensed with dimethylamine, and the product ethylated, giving *ethyl α -dimethylaminoisovalerate*, b. p. about 160° . This was reduced with sodium and alcohol to *dimethylvalinol*, which with methyl iodide gave *valine-choline* in the form of its *iodide*, m. p. 195° . The *aurichloride*, $\text{C}_8\text{H}_{20}\text{ON}\cdot\text{AuCl}_4$, forms yellow leaflets, m. p. 225° ; the *platinichloride*, brownish-red prisms, m. p. $210-211^{\circ}$. Attention is directed to the hindering effect of the *isopropyl* group on the condensation of α -bromoisovaleric acid with dimethylamine.

Attempts to reduce the esters of *N*-acetyl-*L*-tyrosine and *N*-acetyl-*O*-methyl-*L*-tyrosine to amino-alcohols were unsuccessful. *N*-Acetyl-*L*-tyrosine forms white crystals, m. p. 165° ; by methylation with methyl sulphate it gives *N*-acetyl-*O*-methyl-*L*-tyrosine, white needles, m. p. $147-148^{\circ}$. When hydrolysed in acid solution this gives *O*-methyl-*L*-tyrosine, white, glistening leaflets, m. p. 243° ; its *ethyl* ester forms a *hydrochloride*, fine, white needles. *dl*-Tyrosine-choline and its *O*-methyl ether were prepared as follows: α -Bromo- β -*p*-anisylpropionic acid was condensed with dimethylamine and the product esterified, giving *O*-methyl-*N*-dimethyltyrosine ethyl ester, an oil of unpleasant odour, b. p. $165^{\circ}/4$ mm. By reduction this gave *O*-methyl-*N*-dimethyltyrosinol, a nearly colourless oil, b. p. $133^{\circ}/4$ mm. The corresponding choline, *O*-methyltyrosine-choline, forms a crystalline *iodide*, m. p. $137-139^{\circ}$; the *aurichloride* forms large, flat leaves or rosettes of yellow needles, m. p. $112-115^{\circ}$; the *platinichloride*, orange-yellow leaflets, m. p. 204° . By demethylation of the above, *tyrosine-choline* was obtained; its *iodide* forms small, white needles, m. p. 176° ; the *chloride*, small leaflets.

The acetyl derivatives of the synthetic cholines show similar pharmacological behaviour, for instance, in their action on an isolated frog's heart, to ordinary acetylcholine, but greater concentrations are required. When injected intravenously they are much less active than ordinary acetylcholine.

l- α -Dimethyl-leucinol was obtained by the action of magnesium methyl iodide on *L*-leucine ethyl ester. It is an oil of unpleasant

odour, b. p. 187—190°/720 mm.; its *hydrochloride* forms white needles, m. p. 166°, and its *sulphate*, m. p. 237°.

The stearic and palmitic esters of the synthetic cholines show a similar hæmolytic behaviour to those of ordinary choline (cf. Fournéau and Le Page, A., 1914, i, 938). These esters generally show the phenomenon of a double melting point, first melting to oily drops which adhere to the walls of the tube and then becoming fluid at a higher temperature with decomposition. The esters were prepared by the action of the acid chlorides on the choline iodides and chlorides. *l-Leucinecholine iodide stearate*, fine needles, m. p. 108—110° and 138—140°; the corresponding *chloride* forms white needles, m. p. 100° and 120°. *l-Leucinecholine iodide palmitate*, m. p. 105° and 113—115°; corresponding *chloride*, m. p. 100° and 110°. *dl-Phenylalaninecholine iodide stearate*, groups of needles, m. p. 124—125°; corresponding *chloride*, crystal aggregates, m. p. 147° and 172°. *dl-Phenylalaninecholine iodide palmitate*, m. p. 125°; corresponding *chloride*, m. p. 147° and 172°.

E. H. R.

Direct Synthesis of Carbamide starting from Carbon Dioxide and Ammonia. KENNETH C. BAILEY (*Compt. rend.*, 1922, 175, 279—281).—A yield of 14% of carbamide calculated on carbon dioxide was obtained by passing this gas with an excess of ammonia through a quartz tube, heated to redness, and traversed by a concentric glass tube through which cold water was circulated. The carbamide was deposited on the cool walls of the latter, and by using alumina or thoria as catalysts the yield was increased to 19%. By recirculation of the unused carbon dioxide, the yield was further raised to 50% or more. Above 500°, no carbamide was formed, and at 450° only small quantities. As the experiments were conducted at atmospheric pressures and the product was always accompanied by a small amount of ammonium cyanate, ammonium carbamate cannot be considered as an intermediate product of the reaction, which probably takes the course represented by the equations following: (1) $\text{CO}_2 + \text{NH}_3 = \text{H}_2\text{O} + \text{HO-C}\equiv\text{N}$; (2) $\text{HO-C}\equiv\text{N} \rightleftharpoons \text{HN}\cdot\text{CO}$; (3) $\text{HN}\cdot\text{CO} + \text{NH}_3 = (\text{NH}_2)_2\text{CO}$; (4) $\text{HO-CN} + \text{NH}_3 = \text{NH}_4\text{OCN}$.

G. F. M.

Halogenation. XXI. Some Derivatives of Carbamic Esters. Chlorine as a Simultaneous Oxidising and Condensing Agent. RASIK LAL DATTA and BIBHU CHARAN CHATTERJEE (*J. Amer. Chem. Soc.*, 1922, 44, 1538—1543).—When chlorine is passed into a solution of a carbamic ester in methyl alcohol, the latter is oxidised to formaldehyde, which then condenses with two molecular proportions of the ester, giving a methylenediacarbamic ester. A similar reaction occurs in benzyl-alcoholic solution. With ethyl alcohol, simultaneous chlorination and oxidation of the alcohol occurs, with ultimate production of a dichloroethylenecarbamic ester. With substituted urethanes containing an aromatic nucleus, the latter also undergoes chlorination. Condensations of this type do not occur with secondary alcohols.

The following compounds have been prepared. Ethyl methylenedicarbamate, colourless, silky needles, m. p. 131° ; the methyl ester, $\text{CH}_2(\text{NH}\cdot\text{CO}_2\text{Me})_2$, slender needles, m. p. 124° (cf. Conrad and Hock, A., 1903, i, 607); the *propyl* ester, colourless, silky needles, m. p. 113° ; the *isobutyl* ester, slender needles, m. p. 115° ; the *isoamyl* ester, a colourless, microcrystalline powder, m. p. 80° . Ethyl benzylidenedicarbamate, $\text{CHPh}(\text{NH}\cdot\text{CO}_2\text{Et})_2$, silky needles, m. p. 175° ; ethyl dichloroethylidenedicarbamate,

$\text{CHCl}_2\cdot\text{CH}(\text{NH}\cdot\text{CO}_2\text{Et})_2$, slender needles, m. p. 122° ; methylenedi-*p*-chlorodiphenyldiurethane, $\text{CH}_2[\text{N}(\text{C}_6\text{H}_4\text{Cl})\cdot\text{CO}_2\text{Et}]_2$, colourless needles, m. p. 87° ; methylenedi-tetrachloro-*x*-naphthyldiurethane, $\text{CH}_2[\text{N}(\text{C}_{10}\text{H}_5\text{Cl}_2)\cdot\text{CO}_2\text{Et}]_2$, colourless needles, m. p. 160 – 161° .

Urethane in aqueous solution is converted by chlorine into monochlorourethane, which is hydrolysed slowly by cold water to ethyl 4-chloromethylcyclomethylenehydrazineimide-1:3-dicarboxylate, $\text{CH}_2\text{Cl}\cdot\text{CH}\cdot\text{N}(\text{CO}_2\text{Et})_2 > \text{NH}$, colourless needles, m. p. 143 – 144° (cf. Datta and Gupta, A., 1915, i, 122). The constitution of the substance is established by the isolation of the corresponding acetyl derivative, colourless, granular crystals, m. p. 117 – 118° and imide chloride, $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{N}\cdot\text{CO}_2\text{Et})_2\text{NCl}$, unstable, granular crystals, m. p. 75 – 76° .

Methyl dichlorocarbamate is obtained as a yellow liquid by the action of chlorine on an aqueous solution of methyl carbamate.

H. W.

Amide Formation from Esters of Secondary Alkylmalonic Acids. ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1922, **44**, 1564–1567).—Fischer and Dilthey's observations (A., 1902, i, 169) on the difference in the rate of amide formation from ethyl esters of mono- and di-alkylmalonic acids and Meyer's observation (A., 1906, i, 358) on the difference in rate of amide formation from methyl and ethyl esters of dialkylmalonic acids have been extended to include the methyl and ethyl esters of *sec.*-alkylmalonic acids. With respect to amide formation, the secondary alkylmalonic esters are found to resemble the dialkylmalonic esters.

*iso*Propylmalonamide, rhombohedra, m. p. 260° , is prepared by agitating methyl isopropylmalonate with aqueous ammonia (28%) at the atmospheric temperature. Methyl *sec.*-butylmalonate, b. p. 217 – $218^{\circ}/748$ mm. (prepared by the action of methyl alcohol and a little sodium methoxide on the corresponding ethyl ester, b. p. 234 – $236^{\circ}/755$ mm.), is transformed similarly into *sec.*-butylmalonamide, m. p. 242° . On the other hand, the ethyl esters of *isopropyl*- and *sec.*-butylmalonic acids only give small quantities of the corresponding amides after protracted treatment with a large excess of concentrated aqueous ammonia, the greater part of the esters remaining unchanged. Methyl cyclohexylmalonate, b. p. 121 – $122^{\circ}/6$ mm., d_{20}^{25} 1.0737, is prepared in poor yield by the action of ethyl alcoholic sodium ethoxide solution on methyl

malonate and cyclohexyl bromide; it is converted by concentrated ammonia into cyclohexylmalonamide, scaly crystals, m. p. 305°, and a product, needles, m. p. 169°, which is probably the imide. Methyl phenylmalonate gives phenylmalonamide, m. p. 233°.

The ethyl *sec.*-alkylmalonates have been transformed into the corresponding *sec.*-alkylbarbituric acids by treatment with carbamide and an excess of sodium ethoxide at about 105°; 5-*sec.*-butylbarbituric acid, pearly scales, m. p. 199°, 5-cyclohexylbarbituric acid, m. p. 254–256°, and 5-cyclohexyl-2-thiobarbituric acid, small, flat, pale yellow needles, m. p. 188–189°, are described. H. W.

Tautomerism of Dyads. I. Detection of Tautomeric Equilibria in Hydrocyanic Acid. EDITH HILDA USHERWOOD (T., 1922, 121, 1604–1612).

The Action of Organomagnesium Compounds on Nitriles. FRANZ BAERTS (Bull. Soc. chim. Belg., 1922, 31, 184–192).—A study of the action of Grignard's reagent on propionitrile in order to determine whether the latter yields condensation products similar to those obtained from acetonitrile (cf. Bruylants, Bull. Acad. Belg.) and also ketones according to Blaise's reaction (A., 1901, i, 133). With magnesium ethyl bromide, after treatment with water, two substances are obtained from the nitrile, termolecular cyanoethane, (EtCN)₃, and diethyl ketone, the latter in much larger proportion. In addition, a considerable quantity of triethylcarbinol and bimolecular cyanoethane, (EtCN)₂, is formed in the reaction. The bimolecular polymeride, which is the major product in the case of acetonitrile, is in this case about 25% of the total. The formation of the polymerides is explained on the hypothesis that the nitrile acts as a pseudo-acid and schemes are suggested to account for the formation of these and other products.

II. J. E.

Butenonitriles. P. BRUYLANTS (Bull. Soc. chim. Belg., 1922, 31, 175–184).—The preparation of β -butenitrile (vinylacetonitrile) from allyl iodide and cuprous cyanide (Henry, A., 1916, i, 549) need not be carried out under pressure; the reaction takes place with equal ease in the case of allyl bromide, and, in addition, the yield is quantitative. The following physical constants for the substance are given: b. p. 118.4–118.6°/760.5 mm.; m. p. (after solidification in liquid air) 84°; n_D^{20} 1.40297; n_D^{20} 1.40602; n_D^{20} 1.41170; d_4^{20} 0.83409. An isomeride may be obtained by gently heating γ -chlorobutyronitrile and also from the corresponding bromo-compound. Decomposition into the unsaturated nitrile and the halogen acid takes place, but in the latter case β -bromobutyronitrile is formed simultaneously. This isomeride, crotononitrile, may also be obtained from vinylacetonitrile by addition of gaseous hydrochloric or hydrobromic acid and subsequent treatment with potassium hydroxide or pyridine. It consists of a mixture of the two possible stereoisomerides, which can only be separated after repeated fractionation. Physical constants have been determined as follows:—

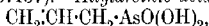
Fraction b. p. 107.6—107.8°, $n_{D_a}^{20}$ 1.41503; n_D^{20} 1.41821; $n_{D_b}^{20}$ 1.42650; d_4^{20} 0.8244; fraction b. p. 120.3—120.5°, $n_{D_a}^{20}$ 1.41835; n_D^{20} 1.42161; $n_{D_b}^{20}$ 1.42985; d_4^{20} 0.8239; and it is on the evidence afforded by these that the author bases his views, as to the space configuration of the substances, as chemical methods of investigation have not, as yet, given any trustworthy indication.

H. J. E.

Possible Asymmetry of Aliphatic Diazo-compounds. II. P. A. LEVENE and L. A. MIKESKA (*J. Biol. Chem.*, 1922, 52, 485—494).—The diazosuccinic ester previously obtained (A., 1921, i, 233) was converted into malic, chlorosuccinic, and bromosuccinic esters. In each case the products had small rotations, thus indicating the existence of optically active diazosuccinic esters. Further work, however, is necessary completely to solve the problem (cf. also Marvel and Noyes, A., 1921, i, 15).

E. S.

Preparation of Allylarsinic Acid. F. HOFFMANN—LA ROCHE & Co., AKT.-GES. (Swiss Pat. 89055; from *Chem. Zentr.*, 1922, ii, 201. Additional to E.P. 167157).—*Allylarsinic acid*,



forms colourless needles or stout prisms, m. p. 129—130°. The white *silver* salt is soluble in dilute nitric acid. The acid decolorises bromine water, and permanganate solution made alkaline with sodium carbonate. The primary *sodium* salt, which forms lustrous leaflets, is not hygroscopic and melts partly at 87—88° in its water of crystallisation. The aqueous solution is weakly acid to litmus and can be heated to 120° without decomposition. The hygroscopic *secondary sodium* salt has an alkaline reaction. The acid is decomposed by mineral acids with the separation of arsenious oxide. The zinc, lead, copper, cobalt, and iron salts are insoluble.

G. W. R.

Preparation of Hydrocarbons. HERMAN PLAUSON and GEORG V. TISCHENKO (D.R.-P. 346065; from *Chem. Zentr.*, 1922, ii, 442).—Carbides which on treatment with water give acetylene, ethylene, or methane are treated, either singly or mixed with steam, at 500—700°. The carbides of calcium, aluminium, manganese, cerium, lanthanum, and uranium are used. With calcium carbide, a mixture of hydrocarbons containing more than 60% of benzene is obtained. A mixture of calcium and aluminium carbides at 600° in a vacuum gives pentinene, whilst at higher pressures polymerised hydrocarbons, for example, terpenes, are obtained.

G. W. R.

The Rôle of Mercuric Nitrate in the "Catalysed" Nitration of Aromatic Substances. II. Nitration of Naphthalene. TENNEY L. DAVIS (*J. Amer. Chem. Soc.*, 1922, 44, 1588—1591; cf. A., 1921, i, 338).—Since naphthalene is very easily nitrated, concentrated nitric acid, even in the presence of mercuric nitrate, converts it promptly into nitronaphthalenes

and the amount of nitronaphthols which is formed is exceedingly small. The best conditions for the production of the latter directly from naphthalene are moderately dilute acid and moderately low temperature. In addition to nitronaphthalenes, 2:4-dinitro- α -naphthol and probably 2-nitro- α -naphthol are produced. The unexpected formation of derivatives of α -naphthol renders the interpretation of the course of the action a matter of considerable difficulty.

H. W.

Preparation of α -Chloronaphthalene Derivatives. KALLE & Co., AKT.-GES. (D.R.-P. 343147; from *Chem. Zentr.*, 1922, ii, 143—144).—Nitronaphthalene- α -sulphonic acids or naphthasultone- α -sulphonic acids are treated with chlorine or chlorinating agents. The sulphonic acid group is thereby replaced by chlorine and chloronitronaphthalenes or chloronaphthasultones are formed. 1-Nitronaphthalene-8-sulphonic acid gives, by the action of chlorine, hydrochloric acid and sodium chlorate, or a hypochlorite, 8-chloro-1-nitronaphthalene. Similarly, from 2-nitronaphthalene-4:8-disulphonic acid, 4:8-dichloro-2-nitronaphthalene is obtained; it forms yellow needles, m. p. 132°. By reduction, 4:8-dichloro-2-aminonaphthalene is obtained; it has m. p. 133°. Chlorination of 1-chloro-5-nitronaphthalene-4-sulphonic acid gives 1:4-dichloro-5-nitronaphthalene. 1:5-Dichloro-4-nitronaphthalene is similarly obtained. Sodium naphthasultone-4-sulphonic acid gives in the same way 4-chloronaphthasultone, m. p. 181—183°. It yields 4-chloro-1-hydroxynaphthalene-8-sulphonic acid by warming with dilute sodium hydroxide solution. This compound gives by hydrolysis 4-chloro-1-hydroxynaphthalene. The products are used in the preparation of colouring matters.

G. W. R.

Preparation of Naphthasultonesulphonyl Chlorides. KALLE & Co., AKT.-GES. (D.R.-P. 343056; from *Chem. Zentr.*, 1922, ii, 144—145).—Naphthasultone or its sulphonic acids are treated with chlorosulphonic acid. In the case of naphthasultone, a sulphonyl chloride group enters the 5-position, whilst in that of the sulphonic acids the sulpho-group is chlorinated. The products are very reactive, and may be used in the preparation of colouring matters. With ammonia or amines, the sultone ring is broken with formation of sulphonamides or amide-substituted sulphonamide derivatives of the corresponding α -naphthalenesulphonic acids. By heating sodium naphthasultone-3-sulphonate with chlorosulphonic acid at 40—100°, naphthasultone-3-sulphonyl chloride is obtained; it forms crystals, m. p. 185°. The corresponding anilide has m. p. 212—213°. Naphthasultone-5-sulphonyl chloride, similarly prepared, forms crystals, m. p. 194°. The anilide has m. p. 146—147°. Naphthasultone-3:6-disulphonyl chloride forms needles, m. p. 163°.

G. W. R.

Hydrogenation of 1:6-Dimethylnaphthalene. FRITZ MAYER and THERESE SCHULTE (*Ber.*, 1922, 55, [B], 2164—2167).—1:6-Dimethylnaphthalene is reduced by sodium and boiling

amyl alcohol to 1:6-dimethyl- $\Delta^{8,7,5}$:8-dihydronaphthalene, b. p. $118^\circ/10$ mm., d^{16}_4 0.9700; the $\beta\beta'$ -position of the double bond in the hydrogenated nucleus is established by the observation that the substance yields a liquid dibromide which regenerates 1:6-dimethylnaphthalene when it is distilled in a vacuum. If the dihydro-compound is reduced by hydrogen in aqueous alcoholic solution in the presence of palladium, 1:6-dimethyl-5:6:7:8-tetrahydronaphthalene, a colourless liquid, b. p. 110 — $111^\circ/10$ mm., d^{16}_4 0.9487, is obtained which is stable towards bromine and is oxidised by nitric acid to benzene-1:2:3-tricarboxylic acid. On the other hand, if 1:6-dimethylnaphthalene is reduced at 240° and 20—25 atmospheres pressure in the presence of a nickel catalyst, it gives a mixture (b. p. 108 — $110^\circ/10$ mm., d^{16}_4 0.9504) of 1:6-dimethyl-1:2:3:4-tetrahydronaphthalene and 1:6-dimethyl-5:6:7:8-tetrahydronaphthalene which is oxidised by nitric acid to a mixture of benzene-1:2:3- and -1:2:4-tricarboxylic acids. H. W.

Constitution of Carbonium Dyes. Halochromism. HUGO KAUFFMANN (*Ber.*, 1922, 55, [B], 1967—1968).—In reply to Hantzsch (this vol., i, 24), the author maintains his priority in the formulation of the triphenylmethane dyes and other halochromic compounds as complex salts. His formulation of carboxylic acids antedates that of Hantzsch by six years. H. W.

The Nature of Carbonium Salts. A. HANTZSCH (*Ber.*, 1922, 55, [B], 2043—2048).—A reply to the criticisms of Fierz (this vol., i, 445), Kehrmann (this vol., i, 331) and Dilthey (this vol., i, 668) (cf. Hantzsch, this vol., i, 24). H. W.

The Fluorene Series. VII. Dibenzofulvene. A. SIEGLITZ and H. JASSOY (*Ber.*, 1922, 55, [B], 2032—2040).—Attempts to transform fluorenyl-9-methylurethane, $\text{CH}(\text{C}_6\text{H}_4)_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, into fluorenyl-9-methylamine have met with considerable difficulty (cf. A., 1921, i, 791), and the further conversion of the latter by Hofmann's degradation into dibenzofulvene, $\text{C}(\text{C}_6\text{H}_4)_2\cdot\text{CH}_2$, appeared not to be realisable. Unexpectedly, it is now found that the urethane can be converted directly into the desired hydrocarbon in small yield.

Dibenzofulvene is prepared by the distillation of fluorenyl-9-methylurethane with calcium oxide in a current of hydrogen under 20—30 mm. pressure. It crystallises in long, colourless needles, m. p. 46 — 48° (51° was observed on one occasion). In substance and in solution it becomes rapidly converted into amorphous products of high melting point. It is oxidised to fluorenone. The corresponding picrate, stable, orange-red crystals, and a colourless, resinous, polymeric dibenzofulvene, m. p. 290° after softening at 255° , are described.

Attempts to prepare 2:7-dibromodibenzofulvene by an analogous method were unsuccessful; the following series of substances was incidentally prepared. Ethyl 2:7-dibromo-9-hydroxyfluorene-9-

acetate (annexed formula), from 2:7-dibromofluorenone, ethyl bromoacetate, and zinc, colourless leaflets, m. p. 106—107°, which is reduced by zinc and hydrochloric acid to 2:7-dibromofluorene-9-acetic acid. 2:7-Dibromo-9-hydroxyfluorene-9-acetic acid, small, colourless needles, m. p. 205—206°. Ethyl 2:7-dibromodibenzofulvene- ω -carboxylate, from the hydroxy-ester at 100°/18 mm., m. p. 172—173°. 2:7-Dibromofluorene-9-acetylhydrazide, colourless needles, m. p. 247—248°, and the corresponding acetonehydrazone, colourless needles, m. p. 234—235°, and benzaldehydehydrazone, colourless needles, m. p. 256—257°. 2:7-Dibromofluorenyl-9-methylurethane, colourless needles, m. p. 191—192°. The latter when distilled with calcium oxide did not appear to yield the corresponding amine or unsaturated hydrocarbon.

In a further series of experiments, 2:7-dibromofluorenone was converted by magnesium and methyl iodide in the presence of ether into 2:7-dibromo-9-hydroxy-9-methylfluorene, colourless prisms, m. p. 162—163°, which was transformed by concentrated hydrochloric acid in the presence of glacial acetic acid into 9-chloro-2:7-dibromo-9-methylfluorene, slender, colourless needles, m. p. 182—183°. The latter gave 2:7-dibromo-9-methylfluorene when distilled under diminished pressure, but was rapidly converted in boiling glacial acetic acid into 2:7-dibromodibenzofulvene, slender, colourless needles, m. p. 205—206°, which may be preserved unchanged for some days in a vacuum. It did not appear to yield a picrate. In a similar manner, 2:7-dibromo-9-hydroxy-9-ethylfluorene, colourless rodlets or coarse prisms, m. p. 133—134°, was transformed successively into 9-chloro-2:7-dibromo-9-ethylfluorene, colourless, lustrous needles, m. p. 171°, and 2:7-dibromo- ω -methylidibenzofulvene, $C(C_6H_5Br)_2 \cdot CHMe$, colourless, woolly needles, m. p. 130—131°, which can be preserved indefinitely. 2:7-Dibromo-9-hydroxy-9-n-propylfluorene crystallises in small, colourless plates, m. p. 150—151°.

2:7-Dibromo-9-hydroxyfluorene, colourless needles, m. p. 168°, is prepared by the reduction of 2:7-dibromofluorenone by aluminium amalgam in the presence of moist ether.

2:7-Dibromofluorene, which has been shown previously (Sieglitz, A., 1920, i, 605) to be an excellent reagent for a series of aromatic acids, can also condense readily with aldehyde acids. Thus, with *o*-phthalaldehyde acid it yields 2:7-dibromo-9-benzylidene-2-carboxylic acid, small, yellow needles, m. p. 224° after softening at 218° (ethyl ester, matted, yellow needles, m. p. 140°), and with opianic acid it gives 2:7-dibromo-9:3':4'-dimethoxybenzylidene-fluorene-2'-carboxylic acid, dull yellow, microscopic rodlets, m. p. 249—250° after previous softening (ethyl ester, large, dark yellow crystals, m. p. 135°; corresponding dihydro-ester, colourless needles, m. p. 90°).

H. W.

Chlorination of *p*-Iododimethylaniline. , GEORG SACHS and LUDWIG LEOPOLD (*Monatsh.*, 43, 1922, 49—53).—Direct chlorination

of *p*-iododimethylaniline in chloroform solution at -12° yields *o*-chlorodimethylaniline-*p*-iododichloride hydrochloride, a yellow, amorphous powder, decomp. $78-85^{\circ}$, which, on reduction by hydrogen sulphide, gives *o*-chloro-*p*-iododimethylaniline, b. p. $159-161^{\circ}/18$ mm., $276-278^{\circ}/760$ mm. (partial decomposition). More vigorous reduction of the iododichloride with zinc dust and hydrochloric acid gives *o*-chlorodimethylaniline. C. K. I.

Preparation of *N*-Nitroso-derivatives of Secondary Amines.

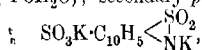
ERICH SCHMIDT and HEINRICH FISCHER (D.R.-P. 343249; from *Chem. Zentr.*, 1922, ii, 202; cf. A., 1920, i, 727-728).—Tetranitromethane is allowed to react with a boiling alcoholic solution of pyridine and a tertiary amine. *o*-Tolylmethylnitrosoamine is prepared from *o*-tolyltrimethylamine, diethylnitrosoamine from triethylamine, and diphenylnitrosoamine from diphenylmethylaniline. Diphenylnitrosoamine forms light yellow crystals, m. p. 66.5° . Nitroform, obtained as a by-product, may be reconverted into tetranitromethane. G. W. R.

Optically Active Amine Oxides. III (iii). Benzylmethylethylamine Oxide. J. MEISENHEIMER and ARTUR LOHSENER (*Annalen*, 1922, 428, 278-285).—Benzylmethylethylamine oxide has been resolved by means of its *d*-bromocamphorsulphonates.

Benzylmethylethylamine, prepared from methylethylamine and benzyl chloride, has b. p. $85-87^{\circ}/10$ mm., forms a *picrate*, m. p. 113° , and an *oxide*, which gives a *dl*-*picrate*, m. p. $106-107^{\circ}$. *l*-Benzylmethylethylhydroxylammonium *d*-bromocamphorsulphonate has m. p. $149-151^{\circ}$, and yields a *l*-*picrate*, m. p. $100-101^{\circ}$, $[\alpha]_D -0.25^{\circ}$. *d*-Benzylmethylethylhydroxylammonium *d*-bromocamphorsulphonate has m. p. $141-143^{\circ}$, and gives a *d*-*picrate*, m. p. $101-103^{\circ}$, $[\alpha]_D +0.25^{\circ}$ (cf. this vol., i, 813). C. K. I.

1:8-Naphthasultam-4-sulphonic Acid and certain of its Derivatives. W. KÖNIG and J. KEIL (*Ber.*, 1922, 55, [B], 2149-2155).—The preparation of 1:8-naphthasultam-4-sulphonic acid and several of its derivatives is described. The sulphonic acid and its anilide are much less reactive towards diazo-compounds than the unsubstituted naphthasultam or α -naphthol-4-sulphonic acid. The tendency towards the formation of *o*-sulphaminydyes is considerably less than towards the formation of the analogous *p*-derivatives and very much less than towards the production of *o*-hydroxyazo-dyes.

1:8-Naphthasultam-4-sulphonic acid, pale pink needles which are very freely soluble in water, is obtained by the action of phosphoryl chloride on potassium α -naphthylamine-4:8-disulphonate at 145° or by the action of sulphuric acid monohydrate on 1:8-naphthasultam alone or in the presence of glacial acetic acid. The primary potassium salt, $\text{SO}_3\text{K}\cdot\text{C}_{10}\text{H}_5\begin{smallmatrix} \text{SO}_2 \\ | \\ \text{NH} \end{smallmatrix}$, almost colourless prisms ($+1.5\text{H}_2\text{O}$); secondary potassium salt,



intensely yellow crystals with green fluorescence ($+H_2O$); secondary barium salt, $C_{10}H_5O_5NS_2Ba \cdot 4H_2O$, and secondary calcium salt, $C_{10}H_5O_5NS_2Ca \cdot H_2O$, are described. 1:8-Naphthasultam-4-sulphonyl chloride crystallises in small, almost colourless leaflets, decomp. above 185° . The corresponding anilide forms colourless plates, decomp. above 230° , whilst the α -naphthalide crystallises in pale brown leaflets, m. p. about 240° (decomp.). Secondary potassium naphthasultam-4-sulphonate couples very slowly with *p*-nitrobenzenediazo hydroxide solution with the formation of 2-*p'*-nitrobenzenazo-1:8-naphthasultam-4-sulphonic acid, long needles, decomp. 280° (the potassium salt is described). 2-*o'*-Methoxybenzenazo-1:8-naphthasultam-4-sulphonic acid crystallises in dark violet leaflets which have no distinct melting point (the potassium salt is described).

H. W.

α -1-Naphthylethylamine. E. SAMUELSSON (*Svensk Kem. Tidsskr.*, 1922, **34**, 7—9).—Naphthyl methyl ketones were prepared in 75% yield by the Friedel-Crafts' reaction; from 50 to 70% of the substance consisted of the α -isomeride, regardless of the temperature of preparation (0 — 50°). In no case was the product the pure α -compound, but when the reaction took place in nitrobenzene, the pure β -form was obtained. α -Naphthyl methyl ketoxime has m. p. 135° , and appears to exist in isomeric forms (cf. Betti and Poccianti, A., 1914, i, 550). α -Naphthylethylamine is a colourless liquid, b. p. 153° , d^{19}_4 1.063; the β -isomeride is a colourless liquid, b. p. 157° . Resolution of the α -isomeride was effected by means of camphoric acid. The *d*-form was not obtained pure; the *l*-form had $[\alpha]^{20}_D$ -80.8° ; and in ethyl alcohol $[\alpha]^{20}_D$ -62.5° . The hydrochloride and oxalate were prepared.

CHEMICAL ABSTRACTS.

The 2-Hydroxy-1-arylnaphthylamines. A. WAHL and R. LANTZ (*Compt. rend.*, 1922, **175**, 171—174).—The halogen atoms in α -chloro- and α -bromo- β -naphthol react readily with aromatic amines with the formation of hydroxyarylnaphthylamines. These are crystalline substances, insoluble in water, soluble in alkali hydroxides, and forming crystalline hydrochlorides, which are dissociated by water. β -Hydroxyphenyl- α -naphthylamine was obtained by boiling α -chloro- or α -bromo- β -naphthol with aniline. It forms white needles, m. p. 155 — 156° . β -Hydroxy- α -*o*-tolyl-naphthylamine, m. p. 114 — 115° , β -hydroxy- α -*p*-tolyl-naphthylamine, white prisms, m. p. 138 — 139° , β -hydroxy- α -*o*-anisyl-naphthylamine, white needles, m. p. 110° , and β -hydroxy- α -(*o*-methoxy-*m*-tolyl)-naphthylamine, white needles, m. p. 118° , were also prepared in a similar way. The methyl ethers of hydroxyphenylnaphthylamine and hydroxy-*p*-tolyl-naphthylamine are also described. The former forms white prisms, m. p. 82 — 83° , and the latter, needles, m. p. 94° .

G. F. M.

Preparation of 1-Arylamino-4-hydroxynaphthalenes. KALLE & Co., AKT.-GES. (D.R.-P. 343057; from *Chem. Zentr.*, 1922, ii, 145).—1:4-Dihydroxy- or 1-amino-4-hydroxynaphthalene

is heated with aromatic amino-compounds. 1-Amino-4-hydroxynaphthalene or its hydrochloride, heated at 180° with aniline, gives 1-anilino-4-hydroxynaphthalene; this forms colourless crystals, m. p. 92° . When dissolved in dilute sodium hydroxide solution and exposed to air naphthaquinoneanil (Euler, A., 1906, i, 369) separates. The hydrochloride forms colourless prisms. The methyl ether, $C_{10}H_7(OMe)NPh$, crystallises in platelets, m. p. 139° . 1-*op*-Dichloroanilino-4-hydroxynaphthalene, prepared from 1:4-di-hydroxynaphthalene and 2:4-dichloro-1-aminobenzene, forms colourless needles, m. p. 73° . 1-*p*-Chloroanilino-4-hydroxynaphthalene (from *p*-chloroaniline) has m. p. 96° . 1-*p*-Toluidino-4-hydroxynaphthalene, m. p. 109° , is prepared from *p*-toluidine. 1-Anilino-4-hydroxynaphthalene-2-carboxylic acid (from anthranilic acid) has m. p. $247-249^{\circ}$. When benzidine is heated with 1:4-dihydroxynaphthalene, it gives 4-amino-1:4'-hydroxynaphthylaminodiphenyl. The products are used in the preparation of colouring matters. By the oxidation of their alkaline solutions coloured compounds of the quinoneanil type are formed.

G. W. R.

Preparation of a Derivative of 2-Amino-5-hydroxynaphthalene-7-sulphonic Acid. KALLE & CO., AKT.-GES. (D.R.P. 342733; from *Chem. Zentr.*, 1922, ii, 202-203).—2-Amino-5-hydroxynaphthalene-7-sulphonic acid (2 mols.) is heated with *p*-phenylenediamine (1 mol.) in the presence of sodium hydrogen sulphite. For example, by heating at 105° in the presence of sodium hydrogen sulphite and sodium hydroxide for twelve hours and cooling, crystalline condensation products separate which are freed from sodium hydrogen sulphite by heating with hydrochloric acid. 1:4-Di(5'-hydroxy-7'-sulpho-2'-naphthylamino)benzene is formed with elimination of ammonia. This compound differs from 2:4'-aminophenylamino-5-hydroxynaphthalene-7-sulphonic acid in that it does not form a crystalline sodium salt or give a coloration with a nitrite and alkaline resorcinol solution.

G. W. R.

Auto-oxidation. Anti-oxygens, and Various Phenomena Related Thereto. II. CHARLES MOUREU and CHARLES DUFRAISSE (*Compt. rend.*, 1922, 175, 127-132).—As previously recorded (this vol., i, 250), the auto-oxidation of many substances is checked by the presence of traces of certain compounds, notably phenols, to which the name anti-oxygens was given. Quantitative experiments have now been made to compare the inhibitive effect of proportions of phenols varying from 1 in 10 to 1 in 1,000,000 on the rate of the absorption of oxygen by acetaldehyde. The measurements were made by observing the rate of the ascension of the mercury column in barometer tubes charged with the reagents, and comparing with a control containing only acetaldehyde and oxygen. Quinol was the most effective phenol in suppressing auto-oxidation, as little as 1 in 100,000 having a very marked effect. Slightly less active were pyrogallol and catechol, followed by resorcinol and 1:3:4-trihydroxybenzene. At a concentration of 1 in 400, phloroglucinol has a maximum retarding effect, but at certain concentrations it actually accelerates

oxidation. Attention is directed to various well-known phenomena which may be attributed to anti-oxygens, for example, to the action of sulphurous gases in preventing the luminescence of phosphorus in dilute oxygen, the action of benzyl alcohol, glycerol, phenol, etc., in retarding the oxidation of sulphite solutions, the prevention of the oxidation of synthetic caoutchouc by phenols, the improved keeping property of essential oils as such, compared with that of the auto-oxidisable substances they contain, when isolated in a pure condition, etc.

G. F. M.

Chemistry of Terpenes, Phytosterols, and Resins. I. Extraction of Amyrin. K. ALB. VESTERBERG (*Annalen*, 1922, **428**, 243—246).—Historical and bibliographical.

C. K. I.

Chemistry of Terpenes, Phytosterols, and Resins. II. Separation of α - and β -Amyrin. Preparation of α -Amyrilene. K. ALB. VESTERBERG and S. WESTERLIND (*Annalen*, 1922, **428**, 247—251).—Details are given for the preparation of crude amyrin, $C_{30}H_{48}OH$, for its separation into α - and β -amyrin by fractional crystallisation of the benzoates, and for the preparation of α -amyrilene, $C_{30}H_{48}$, by the action of phosphorus pentachloride on α -amyrin.

C. K. I.

The Reduction of some Aromatic Compounds by means of Sodium and Absolute Alcohol. HERVÉ DE POMMEREAU (*Bull. Soc. chim.*, 1922, **33**, 689—697; cf. A., 1921, i, 567; Bouveault and Blanc, A., 1903, i, 673).—As a result of the reduction of ethyl benzoate, benzyl alcohol, benzaldehyde, nitrobenzene, ethyl α -naphthoate and α -naphthylcarbinol in order to study the effect of substituents in the ring on the reaction, the author shows that the benzene ring is easily reduced to hexahydrogenated derivatives when it is directly united to a carboxyl group, and that when that group is esterified the reduction is incomplete, some tetrahydrogenated compounds being produced. On the other hand, reduction of naphthalene derivatives takes place readily, as does that of a primary alcohol group directly attached to the aromatic nucleus. The following have been prepared: *tetrahydrobenzyl alcohol* is a colourless liquid, b. p. $188^{\circ}/760$ mm.; α -naphthyl acetate has b. p. $175^{\circ}/18$ mm.; di- α -naphthyl ether forms small, white crystals, m. p. 118° .

H. J. E.

The Decomposition of Proteinogenous Cholines into Alcohols of the Cinnamyl Alcohol Type. P. KARRER and E. HORLACHER (*Helv. Chim. Acta*, 1922, **5**, 571—575).—The decomposition of the proteinogenous cholines containing an aromatic nucleus in the β -position to the ammonium group (cf. A., 1921, i, 228, and this vol., i, 813) proceeds with formation of an alcohol of the cinnamyl type and trimethylamine. The course of the reaction is different, therefore, from the decomposition of ordinary choline (Meyer and Hopff, A., 1921, i, 851). Thus phenylalanine-choline gives, by simply shaking in aqueous solution with silver oxide, cinnamyl alcohol, whilst *p*-methoxyphenylalaninecholine gives *p*-methoxycinnamyl alcohol, a pleasant-smelling substance,

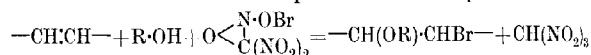
m. p. 73°. The reaction takes place by merely warming the aqueous solution of the choline, the instability of which is probably due to the aromatic nucleus in the β -position to the ammonium group. It is significant that the naturally occurring alcohols of the type, such as cinnamyl alcohol itself, coniferyl alcohol, and syringenin, are all closely related to the naturally occurring amino-acids, from which they may be formed through the cholines. Fresh support is thus given to the hypothesis of choline formation in the plant organism.

E. H. R.

Identity of Xanthosterol with Lupeol. A. J. ULTÉE (*Bull. Jardin Bot. Buitenzorg*, 1922, [iii], 4, 315; cf. Dieterle, this vol., i, 652).—The phytosterol isolated by Dieterle (A., 1920, i, 42) from *Xanthoxylon Budrunga* has been re-obtained, and proves to be identical with lupeol as already suggested by Goodson (A., 1921, i, 488).

Oestling's phytosterol (*Ber. Deut. Pharm. Ges.*, 1914, 24, 308) from *Fagara xanthoxyloides*, Lam. (*X. senegalense*, DC.) is also lupeol.

Bromotrinitromethane. I. ERICH SCHMIDT, WALTER BARTHOLOMÉ, and ALFRED LÜBKE (*Ber.*, 1922, 55, [B], 2099–2107).—The bromine atom can be introduced into the aromatic nucleus of certain compounds, for example, dimethyl-*o*(or *m*)-toluidine by the action of an alcoholic solution of bromotrinitromethane. Addition of alkyl hypobromite at the olefinic bond is effected by the action of bromotrinitromethane on a series of unsaturated substances in the presence of the requisite alcohol



In general, the solution of one molecular proportion of bromotrinitromethane is added gradually to a molecular proportion of the unsaturated compound dissolved in the same solvent; the mixture is preserved in ice water or if necessary heated under a reflux condenser until the smell of bromotrinitromethane disappears after which it is poured into water and extracted with ether after addition of saturated sodium chloride solution. The ethereal solution is subjected to protracted mechanical agitation with sodium hydroxide solution (15%) and twice subsequently with potassium hydroxide solution (15%), to which ultimately a yellow colour must not be imparted; it is then washed with water, and dried over sodium sulphate, after which the desired product is isolated by distillation under diminished pressure. (A second method of operating in the presence of pyridine will be described subsequently.)

The following compounds have been prepared. In so far as they have been described previously their constitution is known, but otherwise more attention has been directed to the applicability of the reaction than to the precise constitution of the products. β -Bromo- α -methoxypropylbenzene (from propenylbenzene), a colourless liquid, b. p. 110–111°/12 mm. β -Bromo- α -ethoxypropylbenzene

a colourless liquid, b. p. 119—120°/13 mm. *o*-Methoxy- β -bromo- α -methoxypropylbenzene, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OMe})\cdot\text{CHBrMe}$, an almost colourless liquid, b. p. 100°/0.2 mm. *o*-Methoxy- β -bromo- α -allyloxypropylbenzene, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{O}\cdot\text{C}_3\text{H}_5)\cdot\text{CHBrMe}$, a pale yellow liquid, b. p. 113°/0.33 mm. *p*-Methoxy- β -bromo- α -methoxypropylbenzene, an almost colourless liquid, b. p. 105°/0.21 mm.; 108°/0.31 mm. *p*-Methoxy- β -bromo- α -ethoxypropylbenzene, b. p. 110—112°/0.21 mm. *p*-Methoxy- β -bromo- α -allyloxypropylbenzene, a pale yellow liquid, b. p. 126—127°/0.3 mm. 3:4-Methylenedioxy- β -bromo- α -methoxypropylbenzene, a pale yellow liquid, b. p. 108—110°/0.14 mm. 3:4-Methylenedioxy- β -bromo- α -ethoxypropylbenzene, b. p. 119—120°/0.2 mm. (if light petroleum or glacial acetic acid is used as solvent, an unstable additive product, $\text{C}_{11}\text{H}_{10}\text{O}_8\text{N}_3\text{Br}$, of isosafrole and bromotrinitromethane is obtained; it has decomp. 100—101°). *Bromocyclohexyl methyl ether* (from cyclohexene), a colourless liquid, b. p. 78—79°/12 mm.; n_D^{20} 1.4910, d_4^{25} 1.3400. *Bromocyclohexyl ethyl ether*, a colourless liquid, b. p. 84—85°/10 mm., n_D^{20} 1.4818, d_4^{25} 1.2751. *Bromocyclohexyl allyl ether*, a colourless liquid, b. p. 100—101°/11 mm. *Bromomethoxy-p-menthan-8-ol* (from terpineol), an almost colourless liquid, b. p. 110—111°/0.42 mm. *Dibromodimethoxy-p-menthane* (from l-limonene), an almost colourless liquid, b. p. 136°/0.3 mm. *Methyl bromomethoxystearate*, b. p. 192°/0.37 mm. *Bromomethoxytetrahydronaphthalene* (from Δ^1 -dihydronaphthalene), a colourless liquid, b. p. 101°/0.31 mm. *Bromomethoxytetrahydronaphthalene* (from Δ^2 -dihydronaphthalene), a colourless liquid, b. p. 115°/0.8 mm. H. W.

Reaction of Carbonyl Chloride with Benzene and *m*-Xylene in the Presence of Aluminium Chloride. ROBERT E. WILSON and EVERETT W. FULLER (*J. Ind. Eng. Chem.*, 1922, **14**, 406—409).—Carbonyl chloride reacts with benzene in the presence of anhydrous aluminium chloride, yielding benzoyl chloride and benzophenone, but no trace of anthraquinone is produced. The reaction takes place in two stages with the intermediate formation of the compound $\text{C}_6\text{H}_5\cdot\text{COCl}\cdot\text{AlCl}_3$, which can be hydrolysed to give benzoic acid; this compound then reacts rapidly with a further quantity of benzene, and the final product is almost entirely benzophenone, irrespective of change of temperature, method of mixing, ratio of reactive substances, etc. When carbon disulphide is used as a diluent a large proportion of the product can be obtained as benzoic acid; this seems to be due to the slight solubility of the intermediate compound in the carbon disulphide, so that it is removed before it can react with more benzene. Reaction between carbonyl chloride and *m*-xylene yields a dixylyl ketone having at least two of the methyl groups in the ortho-position to the carbonyl group; attempts to convert this ketone by oxidation into a derivative of anthraquinone have, so far, not been successful.

W. P. S.

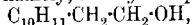
Preparation of *n*-Butyl *p*-Aminobenzoate. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Swiss Pat. 90590; from *Chem. Zentr.*, 1922, ii, 202).—*p*-Aminobenzoic acid is esterified with

n-butyl alcohol, for example in the presence of hydrogen chloride, and heated. On cooling, the *hydrochloride* of the ester crystallises. By addition of alkali hydroxide to an aqueous solution, the free *n*-butyl *p*-aminobenzoate is precipitated. It has *m.* p. 59°, *b.* p. 173—174°/8 mm. (cf. A., 1921, i, 26). G. W. R.

γ -Dibutylaminopropyl *p*-Aminobenzoate. O. KAMM and R. ADAMS (Can. Pat. 217486).—*p*-Nitrobenzoyl chloride dissolved in benzene and γ -dibutylaminopropyl alcohol are heated and the reaction mixture is shaken with excess of tin and hydrochloric acid at a temperature maintained at 50°. The mixture is diluted and the tin removed with hydrogen sulphide. When the aqueous layer is made alkaline, γ -dibutylaminopropyl *p*-aminobenzoate (a local anæsthetic) is precipitated. CHEMICAL ABSTRACTS.

Preparation of Benzyl *p*-Aminobenzoate. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 90587; from *Chem. Zentr.*, 1922, ii, 202).—Compounds containing a *p*-nitrobenzoyl group are benzylated and the resulting benzyl *p*-nitrobenzoate is reduced. For example, dry hydrogen chloride is passed into a benzyl alcoholic solution of *p*-nitrobenzoic acid, or *p*-nitrobenzoates are warmed with benzyl chloride in aqueous solution, or *p*-nitrobenzoyl chloride is heated with benzyl alcohol under a reflux condenser. Benzyl *p*-nitrobenzoate is crystalline. It gives, by reduction with iron and dilute hydrochloric acid, benzyl *p*-aminobenzoate (cf. Shonle and Row, A., 1921, i, 341), which forms white needles, *m.* p. 90°, and acts as a local anæsthetic. G. W. R.

The Reduction of Ethyl α -Naphthylacetate and the α -Naphthylethanols by Sodium and Absolute Alcohol. HERVÉ DE POMMEREAU (*Compt. rend.*, 1922, 175, 105—106).—Ethyl α -naphthylacetate on reduction with sodium in absolute alcohol yielded two products, namely, *tetrahydronaphthylethanol*,



b. p. 187°/25 mm., giving a *phenylurethane*, *m.* p. 91°, and *ethyl tetrahydronaphthylacetate*, from which the free *acid*, *m.* p. 131°, was prepared. Primary α -naphthylethanol, when similarly reduced, gave a *dihydronaphthylethanol*, $\text{C}_{10}\text{H}_9\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, *b.* p. 190°/22 mm., giving a *phenylurethane*, *m.* p. 106°, and secondary α -naphthylethanol gave *ethyl dihydronaphthalene*, *b.* p. 240°/760 mm. W. G.

Fission of $\alpha\alpha$ -Diphenylethyl- β -urethane. A. SIEGLITZ (*Ber.*, 1922, 55, [B], 2040—2042).—The unexpected, direct conversion of fluorenyl-9-methylurethane into dibenzofulvene (Sieglitz and Jassoy, this vol., i, 820) has led the author to investigate the behaviour of the closely similar $\alpha\alpha$ -diphenylethyl- β -urethane under analogous conditions. This substance gives the corresponding amine in the usual manner, the unsaturated hydrocarbon not appearing to be produced.

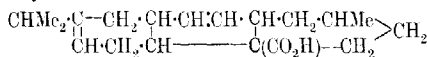
[With HANS SPITZER].—Ethyl $\beta\beta$ -diphenylpropionate is converted by hydrazine hydrate into the corresponding *hydrazide*, colourless, lustrous leaflets, *m.* p. 127—128° (*anisylidene* compound,

colourless needles, m. p. 196°) which is transformed further into the *azide*. The latter is converted by boiling absolute ethyl alcohol into *αα*-diphenylethyl-β-urethane, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}\cdot\text{CO}_2\text{Et}$, colourless needles, m. p. 69° (if aqueous alcohol is used *diphenylethylcarbamide*, slender, colourless needles, m. p. 198°, is also obtained). The urethane is decomposed by distillation with calcium oxide under 12 mm. pressure in an atmosphere of hydrogen into ββ-diphenylethylamine (hydrochloride, m. p. 253°; *picrate*, m. p. 212–213°); the presence of the hydrocarbon, $\text{C}_6\text{H}_5\text{CH}_2$, in the non-basic portion of the distillate could not be established. H. W.

Effect of Attached Groups on the Ease of Formation of the cyclopentane Ring. JUAN PEDIGE CHARLES CHANDRASENA and CHRISTOPHER KELK INGOLD (T., 1922, 121, 1552–1555).

A New Example of Hemihedral Forms not Conforming to the Sign of the Optical Activity. A. DUFFOUR (*Compt. rend.*, 1922, 175, 109–112).—The author records the case of a sample of abietic acid recently isolated by Dupont from the Aleppo pine (cf. A., 1921, i, 510) the goniometric measurements of which conform with those of an abietic acid obtained by Mach from rosin. The specimen was, however, an enantiomorphic form, but did not show opposite optical activity. W. G.

Abietic Acid. A. MADINAVEITIA (*Anal. Fis. Quím.*, 1922, 20, 183–189; cf. Sureda Blanes, A., 1915, i, 493).—The author's analyses lend support to the formula $\text{C}_{19}\text{H}_{28}\text{O}_2$ for abietic acid. The nucleus of the molecule must be retene, since it is obtained by the catalytic dehydrogenation of abietene. The result of hydrogenation of the ethylene linkings by the Willstätter method renders it probable that the carboxyl group in abietic acid is linked to a tertiary carbon atom, and the formula



is suggested.

G. W. R.

Higher Terpene Compounds. V. Conversion of Abietic Acid into Methylretene. L. RZICKA and JULES MEYER (*Helv. Chim. Acta*, 1922, 5, 581–593).—When abietic acid, $\text{C}_{20}\text{H}_{30}\text{O}_2$, is heated with sulphur it is converted into retene (1-methyl-7-isopropylphenanthrene), $\text{C}_{15}\text{H}_{18}$, dehydrogenation being accompanied by loss of a carboxyl group and another carbon atom. Abietic acid is probably therefore a methyldecahydroretenecarboxylic acid, and experiments have been made with the object of determining the orientation of the two groups removable by sulphur. The position of the double linking in abietic acid is unknown, but it is found that dihydroabietic acid also gives retene when heated with sulphur. This practically excludes the possibility of the grouping $\text{C} > \text{CH}=\text{CH}_2$ in abietic acid, the alternative

combination for a mobile carbon atom being $\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \rightarrow \text{C} - \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C} \end{array}$. The

methyl ester of abietic acid and the corresponding alcohol, abietinol, likewise give retene when heated with sulphur. When abietinol is treated with phosphorus pentachloride, a new hydrocarbon, $\text{C}_{20}\text{H}_{30}$, which may be called methylabietin, is obtained which, when dehydrogenated with sulphur, gives a methylretene. Since the methyl group which has replaced the carboxyl group in abietic acid is no longer removable, it is argued that the carboxyl group is not attached to a tertiary carbon atom of the phenanthrene nucleus. Methylretene is oxidised by chromic acid to methylretenequinone. Assuming that the abietic acid skeleton consists, like all known mono- and sesqui-terpene compounds, of isoprene residues (cf. this vol., i, 560, 562), and taking into account the above facts, the only possible positions for the carboxyl and methyl groups under discussion in the phenanthrene nucleus of abietic acid are 2 : 12, 3 : 11, and 4 : 11.

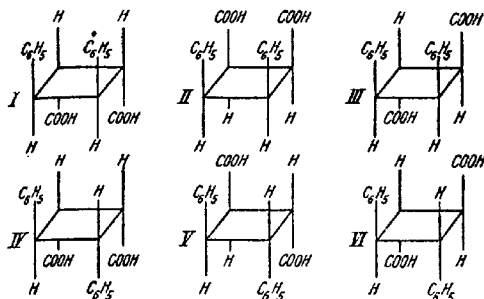
Abietinol, $\text{C}_{20}\text{H}_{32}\text{O}$, prepared by reduction of methyl abietate with sodium and alcohol, has b. p. $169-172^\circ/0.2$ mm., d_4^{20} 1.0305, n_D^{20} 1.5487. *Dihydroabietinol*, by reduction of abietinol with hydrogen in presence of platinum black, forms a colourless, viscous mass, b. p. $169-171^\circ/0.5$ mm. *Methylabietin*, $\text{C}_{20}\text{H}_{30}$, is a viscous, colourless oil, b. p. $147-152^\circ/0.8$ mm., d_4^{20} 0.9750, n_D^{20} 1.54435, $\alpha_D + 56.2^\circ$. It does not form a picrate. Methylretene, $\text{C}_{19}\text{H}_{20}$, forms colourless leaflets, m. p. 79° , and gives an unstable picrate. *Methylretenequinone*, $\text{C}_{19}\text{H}_{18}\text{O}_2$, crystallises in red leaflets, m. p. 147° , and with *o*-phenylenediamine it gives a *quinoxaline*, m. p. 165° . *Retene styphnate* has m. p. 142° . E. H. R.

Preparation of *o*-, *m*-, and *p*-Nitrophenoxyacetic Acids and Various Nitrotoloxycetic Acids and their Derivatives. THOMAS HOSKER MINTON and HENRY STEPHEN (T., 1922, 121, 1591-1598).

The Nitro- and Amino-derivatives of *o*- and *p*-Methoxybenzoic Acids and of α - and β -Methoxynaphthoic Acids. VICTOR FROELICHER and JULIUS BEREND COHEN (T., 1922, 121, 1652-1660).

Configuration of the Truxinic and Truxillic Acids. VI. R. STÖRMER and F. BACHER (*Ber.*, 1922, 55, [B], 1860-1882).—Of the six theoretically possible truxinic acids, four (β -, δ -, ζ -, and neo-) have actually been isolated. The constitution IV has definitely been assigned to ζ -truxinic acid, since this is the only *cis*-acid of the series which is resolvable into its optical antipodes. The β -acid must have the configuration I or II, of which I is the more probable. Both formulæ represent meso-forms and, up to the present, it has not been found possible to resolve the β -acid by alkaloids. The configurations III, V, and VI are available for neo- and δ -truxinic acids, all of which represent resolvable racemic forms. Both acids have now been resolved into their

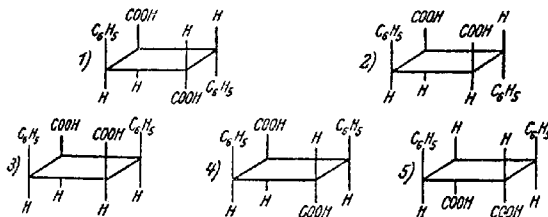
optical antipodes. The δ -acid is closely related to the ζ -acid conversion of δ -acid into the anhydride or imide of ζ -acid; trans-



formation of ζ - into δ -acid in the presence of pyridine, so that the phenyl groups must be in the trans-position to one another in it, thus limiting the choice of the configuration to V or VI. Similarly, neotruxinic acid is related closely to the β -acid, and for it, as a *trans*-acid, only the configuration III is available. The same configurations have been assigned to β -, δ -, and ζ -truxinic acids from considerations based on their formation by the polymerisation of the cinnamic acids on exposure to light. In the authors' opinion, the coincidence is accidental, and de Jong's arguments are not founded on a sufficiently firm theoretical basis.

It is remarkable that δ - and neo-truxinic acids occur in the optically inactive forms in the crude mixture of acids in which they are united to the optically active ecgonine. The technical treatment of the products is not such as would be likely to cause racemisation of the (actually very stable) optically active acids.

In a modified form, the possibility of fission into optically active components can be utilised in elucidating the configuration of the truxillic acids, for which the following formulae are possible:



All these are forms which cannot be resolved into optical antipodes. If dissimilarity is introduced into the carboxyl groups (by conversion of one of them into the ester, amide, anilide, etc.), the forms 1 and 2 become racemic and resolvable, whereas 3, 4, and 5 remain non-resolvable. α - and γ -Truxillic acid anilides

have actually been resolved into their active forms, and therefore must have the configurations 1 and 2. To the γ -acid, which alone yields its proper, stable anhydride, the constitution 2 must be assigned, thus leaving constitution 1 for the α -acid.

Since ϵ -truxillic acid is converted by magnesium phenyl bromide into a ditertiary alcohol, $\text{OH}\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{Ph}_2\cdot\text{CPh}_2\cdot\text{OH}$, which is readily converted into an oxide and by hydrogen bromide into a dibromide which can also be formed from the oxide, it is probable that it is a *cis*-form and not, as previously assumed, a *trans*-acid.

The theoretical portion concludes with a lengthy reply to de Jong (this vol., i, 339) with regard to the nomenclature of the truxillic and truxinic acids.

A more convenient process for the conversion of β - into neo-truxinic acid than that used previously consists in heating the β -acid with concentrated ammonia solution at 170 – 190° , with water at 215° , or alone at 215° . 2.1835 Grams of the acid are soluble in 100 grams of glacial acetic acid at 20° . It is converted quantitatively by molten potassium hydroxide into the δ -acid and by acetic anhydride at 160° into the β -acid. The latter is conveniently identified as the amidic acid, m. p. 194° . The *chloride*, m. p. 83 – 84° , and *dianilide*, m. p. 226 – 227° , of the neo-acid are described. Neotruxinic acid can be resolved by cinchonine in alcoholic solution; the alkaloidal salt of the *d*-acid [m. p. 216 – 217° (decomp.)] being the more sparingly soluble. *d*-Neotruxinic acid has m. p. 236 – 237° , $[\alpha]_D^{20} +52.63^\circ$ in acetone. *l*-Neotruxinic acid, m. p. 236 – 237° , $[\alpha]_D^{20} -53.95^\circ$ in acetone is obtained by treating the acid residues from the resolution of the *r*-acid by cinchonine with quinine in alcoholic solution; *quinine l*-neotruxinate has m. p. 138° . The following derivatives of *d*-neotruxinic acid are described: *chloride*, m. p. 103 – 104° , $[\alpha]_D^{20} -15.98^\circ$ in acetone solution; *dianilide*, m. p. 226 – 227° , $[\alpha]_D^{20} -53.23^\circ$ in acetone; *amide*, m. p. 260 – 261° ; *ethyl ester*, slender needles, m. p. 53° , $[\alpha]_D^{20} +18.33^\circ$ in acetone; *methyl ester*, m. p. 100° , $[\alpha]_D^{20} +48.11^\circ$ in acetone. *l*-Neotruxinic acid yields the following derivatives: *methyl ester*, m. p. 100 – 101° , $[\alpha]_D^{20} -51.99^\circ$ in acetone; *ethylamide*, m. p. 175° , $[\alpha]_D^{20} +30.30^\circ$ in acetone; *methylamide*, slender, matted needles, m. p. 126 – 127° .

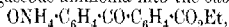
Ammonium δ -truxinate, long, transparent prisms, m. p. 206 – 208° (decomp.) is converted at 215° into ζ -truxinimide, m. p. 168° , which is further identified by its transformation into the ζ -amidic acid, m. p. 222° ; the latter is re-converted by alcoholic potassium hydroxide into the δ -acid. δ -Truxinic acid can be resolved by means of cinchonine in alcoholic solution; *cinchonine l*- δ -truxinate has m. p. 192° . *l*- δ -Truxinic acid, slender needles, m. p. 158 – 159° , $[\alpha]_D^{20} -8.3^\circ$ in acetone, dissolves in glacial acetic acid to the extent of 17.89 parts in 100 at 20° , whereas only 10.38 parts of the *r*-acid dissolve under the same conditions. *d*- δ -Truxinic acid is obtained from the residues of the above resolution by means of quinine. *Quinine d*- δ -truxinate, m. p. 135° (decomp.), is described. *d*- δ -Truxinic acid, m. p. 157 – 158° , has $[\alpha]_D^{20} +8.06^\circ$ in acetone. The following derivatives of *dl*- δ -truxinic acid are described: *chloride*,

m. p. 78° ; *diamide*, colourless crystals, m. p. 224° ; *dianilide*, m. p. 283° ; δ -*truxinic acid*, m. p. 225° . 1- δ -*Truxindiamide* has m. p. 206° , $[\alpha]_D^{25} +33.5^{\circ}$ in acetone.

ζ -*Truxinic acid* is converted by pyridine and water at 195 – 205° into δ -*truxinic acid*, m. p. 175° . H. W.

***o*-4'-Hydroxybenzoylbenzoic Acid and some of its Derivatives.** W. K. ORNDORFF and LOUISE KELLEY (*J. Amer. Chem. Soc.*, 1922, **44**, 1518–1527).—*o*-4'-Hydroxybenzoylbenzoic acid, which in the free condition probably has the lactonic constitution, $\text{HO-C}_6\text{H}_4\text{-C}(\text{OH})\text{-C}_6\text{H}_4$, crystallises in colourless plates, m. p. 213°

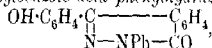
(gas evolution). One hundred c.c. of water, ethyl alcohol (95%), methyl alcohol, and benzene dissolve, respectively, 0.0632, 36.00, 11.58, and 0.0121 grams of the acid at 21° . The acid exhibits an abnormal absorptive power towards dry gaseous ammonia, of which it takes up 2.5 molecular proportions; when placed in an evacuated desiccator over concentrated sulphuric acid, the product loses ammonia slowly and reaches a constant weight when only one molecular proportion of the gas remains. The *ammonium salt*, sodium salt, $\text{C}_{14}\text{H}_9\text{O}_4\text{Na}$, colourless needles (also +1EtOH), the *barium salt*, large, six-sided, greenish-yellow crystals, m. p. 259° (decomp.) after softening at 245° (dihydrate and anhydrous), *calcium salt*, small, pale yellow, glistening needles, m. p. 262 – 263° (decomp.) after softening at 252° (dihydrate and anhydrous), and *zinc salt*, colourless crystals, m. p. 80 – 81° (anhydrous and +7.5H₂O), are described. The *diacetate*, $\text{OAc-C}_6\text{H}_4\text{-C}(\text{OAc})\text{-C}_6\text{H}_4$, prepared by boiling the acid with acetic anhydride and sodium acetate, has m. p. 162 – 163° . *Ethyl o*-4'-hydroxybenzoylbenzoate, $\text{OH-C}_6\text{H}_4\text{-CO-C}_6\text{H}_4\text{-CO}_2\text{Et}$, colourless needles, m. p. 114 – 115° , is converted by dry gaseous ammonia into the substance,



which, however, is not stable, since it loses a part of its ammonia when preserved in a vacuum over sulphuric acid. *Methyl o*-4'-hydroxybenzoylbenzoate, triclinic crystals, m. p. 149 – 150° , similarly absorbs between 1 and 1.5 molecular proportions of ammonia, forming a greenish-yellow semi-liquid mass.

o-3':5'-*Dibromo-4'-hydroxybenzoylbenzoic acid*, colourless crystals, m. p. 250° , is prepared by the bromination of the parent acid in glacial acetic acid solution or (m. p. 246 – 248°) by the action of boiling dilute sulphuric acid on tetrabromophenolphthaleinoxime.

o-4'-Hydroxybenzoylbenzoic acid *phenylhydrazine*,



small, colourless needles, m. p. 267 – 268° , is obtained by heating the acid with an excess of phenylhydrazine at 100° .

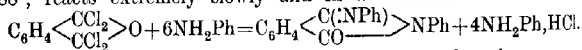
Hydroxyphenylphthalide (cf. Bistrzycki and Oehlert, A., 1894, i, 600; Meyer, A., 1899, i, 707) crystallises in small, colourless needles, m. p. 164 – 165° ; the corresponding acetate, small, colour-

less needles, which probably belong to the triclinic system, has m. p. 125—126°.

o-4'-Methoxybenzoylbenzoic acid is prepared from phthalic anhydride and anisole (m. p. 141.5—142°) or from *o*-4'-hydroxybenzoylbenzoic acid, sodium hydroxide, and methyl sulphate (m. p. 144—145°) (cf. Nourrisson, A., 1886, 1029; Meyer and Turnau, A., 1909, i, 710). The acid absorbs one and a half molecular proportions of dry ammonia gas; the product when preserved in a vacuum over concentrated sulphuric acid ultimately retains one molecular proportion. The *sodium* salt, small, colourless needles, and the *potassium* salt, long, colourless needles (+0.5EtOH), are described. Methyl *o*-4'-methoxybenzoylbenzoate, prepared by the action of sodium hydroxide solution and methyl sulphate on *o*-4'-hydroxybenzoylbenzoic acid, has m. p. 80—81.5° (cf. Meyer and Turnau, *loc. cit.*).
H. W.

The Constitution and Tautomeric Equilibrium of the Two Phthalic Acid Tetrachlorides. ERWIN OTT (*Ber.*, 1922, 55, [B], 2108—2125).—The action of phosphorus pentachloride on ordinary phthalyl chloride at a high temperature has been shown by Vongerichten (A., 1880, 473) to lead to the formation of two crystalline chlorides, $C_6H_4OCl_4$, which he designated phthalic acid tetrachlorides; the formulæ $C_6H_4<\begin{smallmatrix} CCl_2 \\ CCl_2 \end{smallmatrix}>O$ and $CCl_3\cdot C_6H_4\cdot COCl$

were proposed for the compounds, but these were not allocated to the individual substances. Subsequently, Claus and Hoch (A., 1886, 705) could only isolate the isomeride of higher melting point (88°) from phosphorus pentachloride and phthalic anhydride; a similar result was obtained by Anschütz and his pupils in the investigation of the action of phosphorus pentachloride on phthalyl chloride or phthalide. On account of its behaviour in the presence of aluminium chloride and by reason of the intermediate products from phosphorus pentachloride and phthalide, the constitution $CCl_3\cdot C_6H_4\cdot COCl$ has been assigned to the variety, m. p. 88°, by Haller and Guyot (A., 1895, i, 376) and by Anschütz, respectively. This is now shown to be incorrect. The isomeride of lower melting point reacts instantaneously with aniline in suitably concentrated benzene solution with separation of aniline hydrochloride and benzotrichloride-*o*-carboxyanilide: $(CCl_3\cdot C_6H_4\cdot COCl + 2PhNH_2 = CCl_3\cdot C_6H_4\cdot CO\cdot NHPh + NH_2Ph\cdot HCl)$, whereas the substance, m. p. 88°, reacts extremely slowly and in a different manner:



The difference in the rates of reaction is so great that the process can be utilised for the estimation of the chloride of lower melting point in mixtures containing the other isomeride also. For this purpose, the almost quantitatively precipitated mixture of aniline hydrochloride and benzotrichloride-*o*-carboxyanilide is collected, washed with benzene and ether, and weighed; the aniline hydrochloride is removed by water and the residual anilide again weighed.

Towards methyl alcohol, the two chlorides do not exhibit such

marked difference in their behaviour as towards aniline. The isomeride of lower melting point reacts quantitatively in *N*/2 solution in about six hours, in accordance with the equation $\text{CCl}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{COCl} + \text{MeOH} = \text{CCl}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me} + \text{HCl}$. Under similar conditions, the reaction with the lactone is complete in about twenty-four hours according to the scheme $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CCl}_2 \\ \text{CCl}_2 \end{smallmatrix} \text{O} + 4\text{MeOH} = \text{C}_6\text{H}_4(\text{CO}_2\text{Me})_2 + \text{OMe}_2 + 4\text{HCl}$.

Confirmation of the constitutions assigned to the respective chlorides is found in their absorption spectra in the ultra-violet.

Benzotrichloride-*o*-carboxyl chloride reacts much less readily with aniline or methyl alcohol than any 1:2-dicarboxyl chloride hitherto investigated. The behaviour of benzoyl, toluoyl, and mono- and di-chlorotoluoyl chlorides in this respect have therefore been subjected to a comparative examination. Benzoyl chloride reacts far less readily than an aliphatic acid chloride or a true 1:2-dicarboxyl chloride (*s-o*-phthalyl chloride). The presence of a methyl group in the ortho-position causes a somewhat unexpected and considerable increase in reactivity. The introduction of one or two chlorine atoms into the methyl radicle does not diminish the reactivity, which, however, falls far below that of benzoyl chloride when a third chlorine atom is introduced.

A tautomeric equilibrium between the two chlorides tends to become established if one of them is molten. The position of the equilibrium is a function of the temperature; it has been measured at 120°, 220°, and 286.5°. It is thus established that the two forms are mutually interconvertible by alteration of temperature, and that the lactonic cannot be converted into the acyclic form to an extent greater than 80%. The velocity of establishment of equilibrium is readily measurable at the high temperatures and very slow at lower temperatures, and the wandering of the heavier chlorine atom appears therefore to be a much slower process than that of the hydrogen atom. The nature of the equilibrium curve indicates that the acyclic chloride is incapable of existence at temperatures below 70°. This is confirmed to some extent by the observation that, whereas the solid, crystalline material appears stable, the molten substance gradually undergoes transformation at 57.5°. The rate of conversion of the acyclic into the lactonic variety is, however, very small and proceeds much more slowly than the reverse process (the latter is probably subject to catalytic influences).

The two chlorides are prepared in the following manner. Lthalide is heated with phosphorus pentachloride at 100° until action is complete and the phosphorus trichloride and phosphoryl chloride are removed by distillation. The residue is fractionated under 15 mm. pressure. The chloride of higher melting point solidifies from the distillates and is removed. The liquid portions of the distillates and the residues from the crystallisation of the above chloride are united and distilled fractionally in a high *cum*. The initial fractions contain the lactonic chloride, whereas those of highest boiling point are composed of almost

homogeneous acyclic chloride. Benzotrichloride-*o*-carboxyl chloride has m. p. 43° (Vongerichten 47°), b. p. (not definite) 115—120°/0.2 mm., whereas the lactonic form has m. p. 85—86° (Vongerichten 88°), b. p. 90—105°/0.2 mm. Methyl benzotrichloride-*o*-carboxylate has b. p. 125° (corr.)/1 mm. Benzotrichloride-*o*-carboxyanilide has m. p. 165—170° (decomp.). H. W.

Preparation of Phthalimide. BRITISH DYESTUFFS CORPORATION LTD., ARTHUR GEORGE GREEN, and STANLEY JOSEPH GREEN (Brit. Pat. 183044).— α -Nitronaphthalene is directly oxidised by air or oxygen in the presence of a suitable catalyst such as pumice impregnated with an oxide of molybdenum or vanadium and heated at 300—400°, the main product of the oxidation being phthalimide in a yield of upwards of 50% of that theoretically possible. The operation may be carried out by passing a large excess of hot air over nitronaphthalene heated at 120—130°, and thence through a heated iron tube containing the catalyst. Phthalimide condenses in small, colourless needles in a large, well cooled receiver, and a small quantity of phthalic anhydride which is formed, being more volatile, may be collected in a second receiver. G. F. M.

Conditions of Formation of Rings attached to the *o*-, *m*-, and *p*-Positions of the Benzene Nucleus. I. The Action of Sodium on *o*-Phenylenediacetic Ester. WILLIAM HENRY PERKIN, jun., and ALAN FRANCIS TITLEY (T., 1922, 121, 1562—1571).

Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. III. Intra-annular Tautomerism of α -Campholytic Acid. JUAN PEDIGE CHARLES CHANDRASENA, CHRISTOPHER KELK INGOLD, and JOCELYN FIELD THORPE (T., 1922, 121, 1542—1551).

The Dicarboxylic Acid which is Formed by Heating 1:5-Dihydroxynaphthalene with Potassium Hydrogen Carbonate under Pressure. FRANZ HEMMELMAYER (*Monatsh.*, 1922, 43, 61—65).—This acid (cf. A., 1917, i, 227) is probably 1:5-dihydroxynaphthalene-2:6-dicarboxylic acid, because on nitration it gives a *dinitro*-derivative in which the nitro-groups probably occupy α -positions. The substance forms yellow crystals which decompose on heating alone, with water, or with alkalis, and gives characteristic barium salts, $C_{12}H_4O_{10}N_2Ba \cdot 5H_2O$, and $C_{12}H_4O_{10}N_2Ba \cdot 2.5H_2O$. Bromine displaces both carboxyl groups and one nitro-group, giving a *bromonitro*-1:5-dihydroxynaphthalene, whilst acetic anhydride and sodium acetate yield a *dinitro*-1:5-diacetoxynaphthalene, m. p. 205°. Acetic anhydride and sodium acetate convert 1:5-dihydroxynaphthalenedicarboxylic acid into 1:5-diacetoxynaphthalene, m. p. 158—159°. C. K. I.

Formation and Stability of *spiro*-Compounds. VIII. The Dieckmann-Komppa Reaction. FRANK DICKENS, GEORGE ARMAND ROBERT KON, and JOCELYN FIELD THORPE (T., 1922, 121, 1496—1506).

Mellitic Acid, Pyromellitic Acid, and their Production from Carbon by Oxidation. ERNST PHILIPPI (*Annalen*, 1922, 428, 286—287).—A general introduction to the accompanying papers (cf. following abstracts). C. K. I.

Mellitic Acid, Pyromellitic Acid, and their Production from Carbon by Oxidation. I. Oxidation of Carbon by Nitric Acid. ERNST PHILIPPI and GERTRUD RIE (*Annalen*, 1922, 428, 287—295).—A detailed study of this reaction and of the different methods which have been proposed for purifying the product. The preparation of pure mellitic acid by this means is a difficult matter, and the chief value of the method lies in the fact that pyromellitic acid can be obtained in 30% yield from the crude product by heating with sulphuric acid and sodium hydrogen sulphate. C. K. I.

Mellitic Acid, Pyromellitic Acid, and their Production from Carbon by Oxidation. II. Oxidation of Carbon by Sulphuric Acid. ERNST PHILIPPI and RICHARD THELEN (*Annalen*, 1922, 428, 296—300).—Directions are given for the preparation of pyromellitic acid from wood charcoal by oxidation with sulphuric acid in the presence of mercury as catalyst. The yield is 6—7% of the weight of charcoal used [cf. *J. Soc. Chem. Ind.*, 1922, Sept.]. C. K. I.

Mellitic Acid, Pyromellitic Acid, and their Production from Carbon by Oxidation. III. Synthesis of Pyromellitic Acid from Commercial Xylene. ERNST PHILIPPI, REINHARD SEKA, and NORBERT FROESCHL (*Annalen*, 1922, 428, 300—306).—4-Ethyl-*m*-xylene, which is obtained by acetylating *m*-xylene by the Friedel-Crafts' method and reducing the product, gives 6-acetyl-4-ethyl-*m*-xylene, m. p. 27°, on treatment with acetyl chloride and aluminium chloride. The reduction product, 4:6-diethyl-*m*-xylene, b. p. 105°/15 mm., yields pyromellitic acid on oxidation with nitric acid. *m*-Xylene may be replaced by commercial xylene in this series of processes. C. K. I.

Mellitic Acid, Pyromellitic Acid, and their Production from Carbon by Oxidation. IV. Synthesis of Substituted Pyromellitic Acids. ERNST PHILIPPI, REINHARD SEKA, and LILLY ROBINSON (*Annalen*, 1922, 428, 306—313).—A. Nitropyromellitic acids. Pure nitration products of 5-acetyl-2-ethyl-*p*-xylene could not be isolated, but by nitration, followed by oxidation by nitric acid, mono- and di-nitropyromellitic acids were obtained. Nitration of 2:5-diethyl-*p*-xylene gives a small yield of its 3:6-dinitro-derivative, m. p. about 100°, which can be oxidised to dinitropyromellitic acid.

B. Bromopyromellitic acids. 2:5-Diethyl-*p*-xylene can be brominated by sulphur bromide and nitric acid. The product, 3:6-dibromo-2:5-diethyl-*p*-xylene, m. p. 81—82°, on oxidation by nitric acid (d 1.35) at 140°, gives 3:6-dibromo-*p*-xylylene-2:5-diacetic acid, m. p. about 180° (decomp.). 3:6-dibromo-*p*-xylylene-2:5-diglyoxylic acid, m. p. 232°, and dibromopyromellitic acid, decomp. above 170°.

C. K. I.

Preparation of Piperonaldehyde from isoSafrole by the Action of Ozone. SHŌICHIRO NAGAI (*J. Chem. Ind. Japan*, 1922, 25, 631—652).—When ozonised air containing 2—3.5% ozone is introduced into a solution of isosafrole (10 grams) in a perfectly dry solvent (100—150 grams), such as carbon tetrachloride, tetrachloroethane, chloroform, glacial acetic acid, toluene, or xylene, isosafrole ozonide is easily produced. If two to three times the volume of light petroleum, having about the same boiling point as the solvent, is added, the ozonide produced is precipitated; the preparation can therefore be made continuous by adding isosafrole from time to time. The ozonide is a deep reddish-brown, viscous, oily substance having a characteristic odour; it decomposes spontaneously at the room temperature, and its solution is also decomposed by water or by heating at 40—50°. When the ozonide solution is stirred with excess of 35—36% sodium hydrogen sulphite solution, it is decomposed and piperonaldehyde separates as a crystalline additive product in 85% yield.

K. K.

6-Aminoveratraldehyde and its Derivatives. AUGUSTE RILLIET (*Helv. Chim. Acta*, 1922, 5, 547—552).—The preparation of 6-aminoveratraldehyde was accomplished by the same method as that of 6-aminopiperonaldehyde (A., 1921, i, 567), by the reduction of the condensation product of nitroveratraldehyde with an aromatic amine with subsequent hydrolysis. It was not possible, however, thus to reduce 2-nitroveratraldehyde, probably on account of steric hindrance.

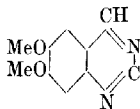
6-Nitroveratrylideneaniline, $\text{NO}_2\cdot\text{C}_6\text{H}_4(\text{OMe})_2\cdot\text{CH:NPh}$, small, brilliant yellow spangles, m. p. 121°, which redden in air, is obtained by condensing molecular proportions of 6-nitroveratraldehyde and aniline; the corresponding o-toluidine compound has m. p. 123°, yellow needles; p-toluidine compound, 131°, p-anisidine compound, 133°. The yields on reduction of these nitro-compounds with sodium sulphide are from 70—80%. 6-Aminoveratrylideneaniline forms yellow spangles, m. p. 119°; of the others, the o-toluidine compound has m. p. 109°, p-toluidine compound, 115°, and p-anisidine compound, 114°. The hydrolysis of the anilino-compounds is somewhat difficult and the conditions have not yet been satisfactorily studied. 6-Aminoveratraldehyde crystallises from a mixture of benzene and light petroleum in long, yellow needles, m. p. 86°; it is immediately coloured red by acids. The acetyl derivative forms white needles, m. p. 176°; benzoyl derivative, yellow needles, m. p. 170°; oxime, colourless spangles, m. p. 148°; phenylhydrazone is greyish-white, m. p. 190°.

By diazotisation, etc., of the amino-aldehyde the following were prepared: 6-chloroveratraldehyde, white needles, m. p. 144°; 6-bromoveratraldehyde, small needles, m. p. 147°; 6-iodoveratraldehyde, white needles, m. p. 128°.

When condensed with acetone, 6-aminoveratraldehyde gives 6:7-dimethoxyquinaldine, yellow crystals, m. p. 103° (hydrochloride, small, white needles, m. p. 232°, mercurichloride, m. p. 250°, picrate, m. p. 217°, platinichloride, m. p. 224°, methiodide,

m. p. 241°). Condensation with methyl ethyl ketone gives 6:7-dimethoxy-2:3-dimethylquinoline, small, colourless, cubic crystals, m. p. 112° (mercurichloride, m. p. 241°, picrate, m. p. 244°, platinichloride, m. p. 226°, methiodide, m. p. 239°). With acetophenone, 6:7-dimethoxy-2-phenylquinoline is obtained, colourless needles, m. p. 131.5° (hydrochloride, m. p. 229°; mercurichloride, m. p. 231—232°; platinichloride, m. p. 208°, methiodide, m. p. 214°).

By heating 6-acetylaminoveratraldehyde with ammonia in a sealed tube at 100° for five hours, a substance was obtained, probably 6:7-dimethoxy-2-methylquinazoline (annexed formula), m. p. 165° (picrate, m. p. 230°). From 6-benzoylamino-veratraldehyde was obtained in the same way 6:7-dimethoxy-2-phenylquinazoline, long, white, silky needles, m. p. 175°; (picrate, m. p. 190°; platinichloride, m. p. 207°). E. H. R.



The Influence of Constitution on the Rotatory Power of Optically Active Substances. XIV. Ketonic Derivatives of 1:2:2:3-Tetramethylcyclopentane and 1:2:2-Trimethylcyclopentane-3-carboxylic Acid. H. RUPE and A. JÄGGI (*Annalen*, 1922, **428**, 164—188).—A number of optically active ketonic and other compounds are prepared from campholic and camphoric acids and their optical constants determined.

1:2:2:3-Tetramethylcyclopentyl phenyl ketone, obtained by the action of magnesium phenyl bromide on campholyl chloride, is a colourless, odourless, strongly refracting oil, b. p. 165°/14 mm. It has d_4^{20} 1.0050; $[\alpha]_D^{20} + 5.72^\circ$, $[\alpha]_D^{20} - 1.21^\circ$, $[\alpha]_{H_2SO_4}^{20} - 12.42^\circ$, $[\alpha]_F^{20} - 50.54^\circ$; n_D 1.52440, n_D 1.52744, n_B 1.53799, n_Y 1.54706; a 10% solution in benzene has d_4^{20} 0.8889, $[\alpha]_D^{20} - 2.70^\circ$, $[\alpha]_D^{20} - 11.47^\circ$, $[\alpha]_{H_2SO_4}^{20} - 23.96^\circ$, $[\alpha]_F^{20} - 66.49^\circ$; and a 10% solution in alcohol has d_4^{20} 0.8051, $[\alpha]_D^{20} + 21.74^\circ$, $[\alpha]_D^{20} + 21.68^\circ$, $[\alpha]_{H_2SO_4}^{20} + 17.51^\circ$, $[\alpha]_F^{20} - 3.73^\circ$. It does not react with semicarbazide, phenylhydrazine, or *p*-nitrophenylhydrazine. On reduction by sodium and alcohol, it yields, in addition to a hydrocarbon, $C_{15}H_{22}$, b. p. 136—137°/12 mm., which has not yet been completely investigated, phenyl-1:2:2:3-tetramethylcyclopentylcarbinol (Rupe and Läger, A., 1920, i, 383). 1:2:2:3-Tetramethylcyclopentyl benzyl ketone is obtained in an analogous way, using magnesium benzyl chloride, and has b. p. 175°/12 mm., d_4^{20} 0.9999, $[\alpha]_D^{20} + 26.46^\circ$, $[\alpha]_D^{20} + 32.16^\circ$, $[\alpha]_{H_2O}^{20} + 36.40^\circ$, $[\alpha]_F^{20} + 42.56^\circ$, n_D 1.51649, n_D 1.51923, n_B 1.52915, n_Y 1.53706; a 10% solution in benzene has d_4^{20} 0.8878, $[\alpha]_D^{20} + 21.51^\circ$, $[\alpha]_D^{20} + 25.91^\circ$, $[\alpha]_{H_2O}^{20} + 28.05^\circ$, $[\alpha]_F^{20} + 33.34^\circ$. 1:2:2:3-Tetramethylcyclopentyl β -phenylethyl ketone has b. p. 182°/13 mm., d_4^{20} 0.9681, $[\alpha]_D^{20} + 13.96^\circ$, $[\alpha]_D^{20} + 23.71^\circ$, $[\alpha]_{H_2O}^{20} + 27.68^\circ$, $[\alpha]_F^{20} + 35.43^\circ$; a 10% solution in benzene has d_4^{20} 0.8870, $[\alpha]_D^{20} + 14.32^\circ$, $[\alpha]_D^{20} + 18.15^\circ$, $[\alpha]_{H_2O}^{20} + 20.86^\circ$, $[\alpha]_F^{20} + 27.40^\circ$. 1:2:2:3-Tetramethylcyclopentyl α -naphthyl ketone has m. p. 78°, b. p. 229°/14 mm.; a 10% solution in benzene has d_4^{20} 0.8939, $[\alpha]_D^{20} - 41.95^\circ$, $[\alpha]_D^{20} - 60.52^\circ$, $[\alpha]_{H_2O}^{20} - 80.21^\circ$, $[\alpha]_F^{20} - 132.25^\circ$; a 5% solution in alcohol has d_4^{20} 0.8012, $[\alpha]_D^{20} - 12.23^\circ$, $[\alpha]_D^{20} - 19.97^\circ$, $[\alpha]_{H_2O}^{20} - 29.45^\circ$, $[\alpha]_F^{20} - 58.16^\circ$.

Methyl 1-acetyl-1 : 2 : 2-trimethylcyclopentane-3-carboxylate is obtained from α -methyl camphoryl β -chloride [$C_8H_{14}(COCl) \cdot CO_2Me$] and zinc methyl or methyl iodide and magnesium. It has b. p. $130-131^\circ/12$ mm., d_4^{20} 1.0430, $[x]_D^{20} -10.53^\circ$, $[x]_D^{25} -14.02^\circ$, $[x]_{D_5}^{20} -14.08^\circ$, $[x]_{FeCl_3}^{20} -17.39^\circ$, $[x]_{Fe}^{20} -24.99^\circ$; n_D 1.46729, n_D 1.46857, n_D 1.47554, n_D 1.48039; a 10% solution in benzene has d_4^{20} 0.8919, $[x]_D^{20} -14.46^\circ$, $[x]_D^{25} -19.17^\circ$, $[x]_{D_5}^{20} -20.18^\circ$, $[x]_{FeCl_3}^{20} -23.43^\circ$, $[x]_{Fe}^{20} -33.41^\circ$. The *semicarbazone* crystallises in white leaflets, m. p. 194° . On attempting to condense the ketonic ester by Dieckmann's method, a substance, $C_{22}H_{32}O_4$, m. p. $221-222^\circ$, giving a *silver* salt, $C_{22}H_{30}O_4Ag_2$, was obtained; on treating the ketonic ester with dry hydrogen chloride, a substance, $C_{17}H_{26}O_2$, was obtained as a mobile oil, b. p. $139-141^\circ$, which solidified to needles, m. p. 85° ; definite structures are not assigned to these substances. *1-Acetyl-1 : 2 : 2-trimethylcyclopentane-3-carboxylic acid*, m. p. 90° , b. p. $177/9$ mm., is obtained by hydrolysis of the ester; a 5% solution in benzene has d_4^{20} 0.8874, $[x]_D^{20} +84.29^\circ$, $[x]_D^{25} +109.98^\circ$, $[x]_{D_5}^{20} +116.07^\circ$, $[x]_{Fe}^{20} +133.20^\circ$, $[x]_{Fe}^{25} +185.71^\circ$. The *semicarbazone* forms minute nodules, m. p. 224° , and the *oxime*, needles, m. p. $165-166^\circ$.

C. K. I.

Transformation Products of 1-Methyl-1-trichloromethyl- $\Delta^{2:3}$ -cyclohexadiene-4-one. K. VON AUWERS and W. JÜLICHER (*Ber.*, 1922, 55, [B], 2167-2191).—1-Methyl-1-trichloromethyl- $\Delta^{2:3}$ -cyclohexadiene-4-one, $O: \langle \text{cyclohexadiene ring} \rangle \begin{matrix} \text{Me} \\ \text{CCl}_3 \end{matrix}$, has been prepared by

Zincke and Suhl (*A.*, 1907, i, 37), and its properties have been investigated further by Zincke and Schwabe (*A.*, 1908, i, 337). In structure, it is closely similar to 1-methyl-1-dichloromethyl- $\Delta^{2:3}$ -cyclohexadiene-4-one, described by von Auwers (*A.*, 1907, i, 399). The investigation of the former substance has been extended so as to permit an exact comparison of the two products. In their general behaviour, the trichloroketone and dichloroketone are very closely similar, differences being observed only in minor points. Each substance exhibits a very pronounced tendency to pass directly or indirectly into aromatic compounds, whereby either the chloromethyl or the methyl group wanders, depending on the particular reagent used and the substance under investigation.

1-Methyl-1-trichloromethyl- $\Delta^{2:3}$ -cyclohexadiene-4-one yields a *semicarbazone*, colourless, lustrous needles, m. p. $197-198^\circ$, and a *p-nitrophenylhydrazone*, yellow plates, m. p. $159-160^\circ$. The oxime is remarkably stable towards acids and, probably for this reason, its transformation could not be effected. The trichloroketone is converted by phosphorus pentachloride into 4-chloro-*o*-methylbenzotrichloride, which is identified by converting it into *p*-chloro-*o*-toluic acid, m. p. $166-167^\circ$.

1 : 4-Dimethyl-1-trichloromethyl- $\Delta^{2:3}$ -cyclohexadiene-4-ol, m. p. $131-132^\circ$ (the stability of the substance when preserved appears to depend largely on the freedom of the atmosphere from acid vapours), is smoothly converted at 35° in light petroleum solution in an atmosphere of hydrogen into 1-methyl-1-trichloromethyl-4-

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methylene- $\Delta^{2:5}$ -cyclohexadiene, $\text{CH}_2 \cdot \begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array} \begin{array}{c} \text{Me} \\ \text{CCl}_3 \end{array}$, a pale yellow liquid which decomposes rapidly on exposure to air, d_4^{20} 1.2022, d_4^{20} 1.202, n_D^{16} 1.55171, n_D^{19} 1.55710, n_D^{19} 1.56986, n_D^{20} 1.5569. Methyl-*p*- $\beta\beta$ -trichloroethylbenzene is conveniently obtained by heating the carbinol in boiling glacial acetic acid solution. The carbinol is converted by ice-cold concentrated sulphuric acid into 2:4-dimethylbenzoic acid.

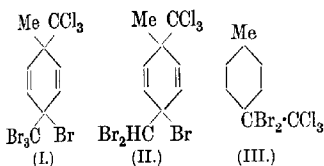
4-Phenyl-1-methyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-ol, m. p. 120—121°, loses water when dissolved in ice-cold formic acid and yields a viscous, yellow liquid from which hydrogen chloride is continuously evolved at the atmospheric temperature; if the liquid is distilled under diminished pressure, it gives 4-ethyl-diphenyl, unctuous plates, m. p. 46—47°, b. p. 140°/15 mm. in small quantity (the constitution of the substance follows from its preparation by the reduction of 4-acetyldiphenyl with zinc and hydrochloric acid). The carbinol is converted by sulphuric and glacial acetic acids into 4-phenyl-2-methylbenzoic acid, m. p. 168—169°, the calcium salt of which is converted by distillation with lime into 3-methyldiphenyl, a pale yellow liquid, b. p. 272—274°, $d_4^{16.7}$ 1.0182, d_4^{20} 1.015, $n_D^{16.7}$ 1.59747, $n_D^{16.7}$ 1.60443, $n_D^{16.7}$ 1.62386, n_D^{20} 1.6029. 4-Phenyl-2-methylbenzoic acid is oxidised by permanganate to diphenyl-3:4-dicarboxylic acid, m. p. 194° (anhydride, colourless needles, m. p. 135—136°).

The trichloro-ketone is transformed by ethyl bromoacetate and zinc in the presence of benzene (which must be freed from sulphur compounds by protracted treatment with aluminium chloride) into ethyl 1-methyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-ol-4-acetate, $\text{Me} \cdot \begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array} \begin{array}{c} \text{OH} \\ \text{CH}_2\text{-CO}_2\text{Et} \end{array}$, a dark-coloured liquid containing considerable amounts of unattacked ketone, which is hydrolysed to 1-methyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-ol-4-acetic acid, colourless, slender needles, m. p. 125—126° (decomp.). The ester loses water under the influence of ice-cold formic acid, but the residual hydroaromatic ester could not be purified satisfactorily. The acid is converted by being heated in xylene solution or on the water-bath into $\beta\beta\beta$ -trichloro- α -*p*-tolylpropionic acid, small, colourless plates, m. p. 168.5—169.5°. The hydroxy-acid is converted by energetic treatment with alcoholic potassium hydroxide solution into $\beta\beta$ -dichloro-*p*-methylatropic acid, $\text{CCl}_2\text{C}(\text{C}_6\text{H}_4\text{Me})\text{-CO}_2\text{H}$, slender, colourless needles, m. p. 118.5—120°. The action of concentrated sulphuric acid on the hydroxy-acid leads to the formation of 4-carboxy-3-methylphenylacetic acid, colourless leaflets, m. p. 198.5—199.5°.

The trichloro-ketone reacts less readily than the dichloro-ketone with chlorine. If, however, a slow stream of chlorine is passed into a solution of the former in carbon tetrachloride containing iodine, an unstable dichloride is produced which passes slowly when preserved, rapidly when boiled with acetic acid and potassium acetate, into 3-chloro-1-methyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-

4-one, small, colourless needles, m. p. 99° (*oxime*, colourless needles, m. p. 162—164°, *p*-nitrophenylhydrazone, yellow needles, m. p. 146—148°). When dissolved in carbon disulphide and treated with chlorine in direct sunlight, the trichloro-ketone is transformed into 2:3:5:6-tetrachloro-1-methyl-1-trichloromethylcyclohexane-4-one, small, colourless needles, m. p. 134—136°, which is converted by cautious treatment with sodium hydroxide solution into 3:5-dichloro-1-methyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-one, small, lustrous plates, m. p. 161—162°.

3:5-Dibromo-1-methyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-one (cf. Schwabe, *loc. cit.*), m. p. 172°, is prepared conveniently by exposing a solution of the trichloro-ketone in an excess of bromine to bright sunlight and subsequently evaporating the solution to dryness. When dissolved in benzene and treated with an ethereal solution of magnesium methyl bromide, it is converted into 3:5-dibromo-1:4-dimethyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-ol, colourless needles, m. p. 88—95°, which probably consists of a mixture of stereoisomeric forms. The carbinol loses water with



Zincke and his co-workers by the bromination of the methyl-carbinol indicates that bromine is not present in the nucleus of the latter substances. Zincke's tetra-, tri-, and di-bromo-compounds receive the formulæ I, II, and III, respectively.

some difficulty, and passes into 3:5-dibromo-1-methyl-1-trichloromethyl-4-methyl-ene- $\Delta^{2:5}$ -cyclohexadiene, m. p. (indefinite) 83—100°. The dissimilarity of the latter substance and the dibromo-compound obtained by H. W.

The Action of Alcohols on α -Bromobenzylideneacetophenone. CH. DUFRAISSE and P. GÉRALD (*Compt. rend.*, 1922, 174, 1631—1632).—It has previously been shown (this vol., i, 39) that ethyl alcohol condenses with α -bromobenzylideneacetophenone to give a saturated compound, which with an alkali hydroxide loses hydrogen bromide to give an ethylenic compound. This is now shown to occur with other alcohols, and new compounds described are: α -bromo- α -benzoyl- β -methoxy- β -phenylethane, $\text{CHBzBr} \cdot \text{CHPh} \cdot \text{OMe}$, m. p. 76—77°; α -bromo- α -benzoyl- β -propoxy- β -phenylethane, m. p. 95—96°; α -bromo- α -benzoyl- β -butoxy- β -phenylethane, m. p. 81—82°; α -bromo- α -benzoyl- β -isobutoxy- β -phenylethane, m. p. 110—111°; α -benzoyl- β -methoxy- β -phenylethylene, $\text{CHBz} \cdot \text{CPh} \cdot \text{OMe}$, m. p. 65—66°; α -benzoyl- β -propoxy- β -phenylethylene, m. p. 59—60°; α -benzoyl- β -butoxy- β -phenylethylene; α -benzoyl- β -isobutoxy- β -phenylethylene, m. p. 55—56°, and α -benzoyl- β -isopropoxy- β -phenylethylene, m. p. 49—50°.

W. G.

The Grignard Reaction. G. J. ÖSTLING (*Hyllningsskrift tillägnad Ossian Aschan*, 1920, 92—97).—An attempt was made to prepare ketones by means of the Grignard reaction. Magnesium

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phenyl bromide reacted with benzyl chloride, giving a trace of benzophenone. All other experiments gave negative results.

CHEMICAL ABSTRACTS.

Imino-aryl Ethers. I. N-Phenylbenzlimino-*m*-hydroxyphenyl Ether and the Synthesis of 2:4-Dihydroxybenzophenone. ARTHUR WILLIAM CHAPMAN (T., 1922, 121, 1676-1681).

Dinitrobenzil. E. DE BARRY BARNETT and L. J. KAY (*Chem. News*, 1922, 125, 57-58).—Dinitrobenzil may be obtained in almost theoretical yield and very pure by nitration of benzil with a mixture of sulphuric and nitric acids. Details of the preparation are given. Although dinitrobenzil has two carbonyl groups, it only forms a *monophenylhydrazone*, m. p. 159° (decomp.), under ordinary conditions. Attempts to prepare a tetranitro-derivative from dinitrobenzil by further nitration were unsuccessful. G. W. R.

A Double Decomposition Catalysed by Copper. EDUARD KOPETSCHNI and HERTA WIESLER (*Monatsh.*, 1922, 43, 89-92).—When 1-chloro-2-aminoanthraquinone is boiled with excess of dimethylaniline with the addition of a small amount of copper powder or cupric acetate, a good yield of 2-aminoanthraquinone is produced. The chlorine is presumed to re-enter into combination as *p*-chlorodimethylaniline, which may undergo subsequent reduction to tetramethylbenzidine. If potassium carbonate is added in addition to copper powder or cupric acetate, or if the dimethylaniline is replaced by methylaniline, 2-aminoanthraquinone is not obtained, although indanthrene and flavanthrene can be recognised amongst the products. C. K. I.

Homologues of Menthol. AKIRA OGATA and CHUJI MIYASHITA (*J. Pharm. Soc. Japan*, 1922, 473-482).—By the action of magnesium methyl iodide, menthone is converted into *menthylmenthol* (1:5-dimethyl-2-isopropylcyclohexanol), b. p. 83°/6 mm., d_4^{16} 0.8991, $[z]_D^{20} +9.74^\circ$. When boiled under atmospheric pressure or warmed with zinc chloride, it loses the elements of water and changes into 5-methyl-2-isopropyl-1-methylenecyclohexane, b. p. 181-182°, d_4^{18} 0.8273, $[z]_D^{20} +87.25^\circ$. By the same method, ethyl- and propyl-menthols have been prepared from menthone. When distilled under atmospheric pressure, *ethylmenthol* (5-methyl-1-ethyl-2-isopropylcyclohexanol), b. p. 84-85°/4 mm., d_4^{16} 0.9040, $[z]_D^{20} +10^\circ$, was partly decomposed into menthone (semicarbazone, m. p. 186°). By warming with zinc chloride it gave 5-methyl-2-isopropyl-1-ethylidenecyclohexane, b. p. 58-59°/4 mm., d_4^{16} 0.8304, $[z]_D^{20} +34.70^\circ$. *Propylmenthol* (5-methyl-1-propyl-2-isopropylcyclohexanol) gave, on warming with zinc chloride two isomeric hydrocarbons (1-methyl-4-isopropyl-3-propylenecyclohexane), which are differentiated by the position of the double bond: one, with an odour like that of an ethylidene derivative has b. p. 46-50°/6 mm., $d_4^{16.5}$ 0.8124, $[z]_D^{20} +3.09^\circ$, whilst the other, which is almost odourless, has b. p. 91-92°/11 mm., $d_4^{16.5}$ 0.8318, $[z]_D^{20} +32.43^\circ$. K. K.

Hydration of Caryophyllene. YOSHIHIKO ASAHINA and TAKEO TSUKAMOTO (*J. Pharm. Soc. Japan*, 1922, 463—473).—A mixture of absolute ether and sulphuric acid monohydrate has been used for the hydration of some hydrocarbons by Aschan (Schimmel & Co. Rep., 1919, 130), and is now found to effect hydration of caryophyllene more easily and quickly than Bertram's method (*Annalen*, 1892, 271, 288). One hundred c.c. of caryophyllene were added drop by drop to a mixture of 80 c.c. of absolute ether and 30 c.c. of sulphuric acid monohydrate cooled to 0°, the temperature of the reaction mixture being maintained below 10°. After remaining for one to two hours at the room temperature, it was poured into a mixture of ice and sodium carbonate and the alkaline solution subjected to distillation with steam, when a 30% yield of caryophyllene alcohol, m. p. 94—95°, was obtained. The alcohol has always been regarded as optically inactive, but it is now found to be active, $[\alpha]_D^{20} - 5.8^\circ$ in alcohol. The phenylurethane, m. p. 135°, has $[\alpha]_D^{20} + 50.5^\circ$ in alcohol. An oily by-product which distilled with the alcohol was separated into two fractions:

(a) b. p. 93—98°/3 mm., d^{20}_4 0.9237, $n^{20}_D - 31.76^\circ$, $n^{20}_D 1.5037$, and

(b) b. p. 98—105°/3 mm., d^{20}_4 0.9283, $[\alpha]^{20}_D - 33.68^\circ$, $n^{20}_D 1.4997$.

The alkaline-aqueous solution remaining in the flask in the above distillation was freed from resinous matter by shaking with ether, acidified with dilute sulphuric acid, and distilled with steam, when a substance passed over, crystallising in plates, m. p. 117°, soluble in the ordinary organic solvents, and stable towards permanganate, etc. It proved to be an *isomeride* of caryophyllene alcohol, and is optically inactive, as also is its *phenylurethane*, m. p. 180°. It is therefore regarded as the α -compound and the active one as the β -compound. Clovene was prepared from the β -compound by Wallach's method and found also to be optically active, b. p. 259—260°, d^{20}_4 0.9241, $n^{20}_D 1.49985$, and $\alpha_D + 2.84^\circ$.

K. K.

Essential Oils. ROURE-BERTRAND FILS (*Bull. Sci. Ind.*, 1920, [iv], 1, 1—38, and 2, 1—37; from *Chem. Zentr.*, 1922, i, 359—360).—Scheih oil, from *Artemisia herba-alba* var. *genuina* of Algerian origin, has d^{15}_4 0.9432; $[\alpha]_D^{20} + 2^\circ 6'$; acid number, 3.5; saponification number, 57.4; ester number, 53.9; acetyl number, 147; combined alcohols, 14.80%; free alcohols, 30.64%. A sample kept for six years gave a greater acid number and on distillation with steam yielded 70% of an oil with properties different from those of the fresh oil. Camphor, cineole, and l-camphor were found as constituents, also, from the odour, menthol (cf. Grimal, A., 1904, i, 605). Gouft oil, from *Artemisia campestris*, L., var. *odoratissima*, has d^{15}_4 0.8727; $[\alpha]_D^{20} - 16^\circ 20'$; acid number, 0.94; saponification number, 30.81; ester number, 29.87; acetyl number, 41.07; combined alcohols, 8.21%; free alcohols, 3.44%. It does not change appreciably on keeping. The constituents found were l- α -pinene, nopinene (?), and geraniol (cf. Jeaneard and Satic, A., 1904, i, 516). Pagoda corn oil from Annam of unknown botanical origin has d^{20}_4 0.9182, $[\alpha]_D^{20} + 58^\circ 40'$; $n^{20}_D 1.4870$; acid

number, 1-87; saponification number, 11-20; ester number, 9-33; acetyl number, 130-67; total alcohol ($C_{10}H_{18}O$), 39-83%; combined alcohols, 2-56%. The constituents are *d*-limonene, geraniol (?), and cuminaldehyde. Rhododendron oil from *R. ferrugineum* has d^{15} 0-840; acid number, 0-0; saponification number, 63-47 (cf. Haensel, A., 1906, i, 524). Pichurim bean oil, from the seeds of *Nectandra Puchury major*, is yellowish-green in colour and has d^{17} 1-0396; $[\alpha]_D -4^{\circ} 54'$; n_D^{18} 1-5180; acid number, 2-8; saponification number, 2-8; acetyl number, 33-47. It contains 8% of phenols, including isoeugenol. Safrole and cineole are present. The oil obtained by extraction of the distillation water has d^{15} 1-0237; $[\alpha]_D -9^{\circ} 28'$; acid number, 9-33; saponification number, 9-33. *Cistus ladaniferus*, L., and *C. Monspeliensis* give an oil with $d^{17.5}$ 0-9033; $[\alpha]_D -12^{\circ} 10'$; $n_D^{17.5}$ 1-4800; acid number, 3-7; saponification number, 22-37. The distillation water yields on extraction with light petroleum an oil having $d^{17.5}$ 0-9755, $[\alpha]_D -2^{\circ} 40'$; acid number, 18-67; saponification number, 41-07. The essential oil from *Chenopodium ambrosioides* (Dutch Indies) has d^{15} 0-9763; acid number, 0-93; saponification number, 7-47. The corresponding oil from the distillation water has d^{15} 0-9843; acid number, 0-93; saponification number, 13-98. It has been found specific against ankylostomiasis. The essential oil from *Skimmia laureola* is light green in colour and has d^{15} 0-8931; $[\alpha]_D^{15} +4^{\circ} 28'$; saponification number, 82-13. Cinnamon oil (Annam) has d^{15} 1-051; n_D^{15} 1-690; $[\alpha]_D -0^{\circ} 8'$; acid number, 2-8; aldehydes, 95%.
G. W. R.

Two Indo-Chinese Oils. ROURE-BERTRAND FILS (*La Parfumerie Moderne*, 1921, 14, 151; from *Chem. Zentr.*, 1922, i, 360).—Pagoda corn oil has a similar odour to geranium and bergamot. It has d^{20} 0-920; $[\alpha]_D +56^{\circ} 8'$; n_D^{20} 1-4870; saponification number, 13-25; acetyl number, 139-13; free alcohol, 38-20%. Limonene and geraniol are present (cf. preceding abstract). Annam brier oil has an odour like cajuput oil. It has d^{20} 0-886; $[\alpha]_D -0-6^{\circ}$; n_D^{20} 1-4772; ester number, 10-45; acetyl number, 50-21; free alcohols, 11-27%. It is probably obtained from *Cathetus fasciculata*, Lour.
G. W. R.

Essential Oils. ROURE-BERTRAND FILS (*Bull. Sci. Ind. Roure-Bertrand Fils.*, 1921, [iv], No. 3, 14—19; from *Chem. Zentr.*, 1922, ii, 483).—Boldo leaf oil, the essential oil from the leaves of *Peumus Boldus*, Mol., has d^{17} 0-9318, d^{15} 0-9334; $[\alpha]_D -0-14^{\circ}$; acid number, 1-87; saponification number, 14-87; it contains 30% of cineole. The oil from the distillation water has d^{15} 0-9323; acid number, 3-73; saponification number, 26-13; acetyl number, 142-18. It has a different odour from that of the first oil and contains 15% of phenols. Patchouli oil (Sumatra) from the leaves has d^{15} 0-9689; $[\alpha]_D -52^{\circ} 4'$; acid number, 1-2; saponification number, 7-9; acetyl number, 26-13. Patchouli oil from the stems has d^{15} 0-9739; $[\alpha]_D -54^{\circ} 8'$; acid number, 8-7; saponification number, 10-0.
G. W. R.

Essential Oils. ROURE-BERTRAND FILS (*Sci. Ind. Bull.*, 1921, [iv], No. 4; cf. A., 1921, i, 797, 798).—An oil distilled from *Lavandula stoechas* resembled that ascribed by Schimmel & Co. (1905) to *L. dentata*. It had d^{15} 0.945–0.962, α $+35^{\circ} 30'$ to $+47^{\circ}$, acid number, 0.93–5.16; saponification number, 18.26–18.67; ester number, 13.1–17.74; acetyl ester number, 47.14. The chief constituents (80%) are *d*-camphor and *d*-fenchone, probably also fenchyl alcohol, terpineol, and a phenol compound. *d*-Fenchone has d^{20} 0.9443, d^{26} 0.9402, $\alpha^{23} +54^{\circ} 34'$, n_D^{25} 1.4625, m. p. $3-5^{\circ}$. Oil of angelica root, obtained by distilling the fresh root with water, had $d^{17.5}$ 0.8887, d^{15} (corr.) 0.8907, $\alpha^{18} +6^{\circ} 42'$ (normally 16° to $+41^{\circ}$), acid number, 7.20 (usually 1 to 4); saponification number, 52.27 (13 to 44); ester number, 45.07 (12 to 40). Madagascar cinnamon bark oil (a) from pounded bark, (b) from the separated water by extraction with light petroleum, (c) a mixture of both, had respectively d^{17} 0.9715, 1.0281, 1.0075; d^{15} 0.9731, 1.0297, 1.0091; $\alpha^{17} -5^{\circ} 49'$, $\alpha^{16} -2^{\circ} 2'$, $\alpha^{17} -3^{\circ} 23'$; acid number, 2.49; 2.49, 2.49; aldehyde content, 48%, 82%, 70%. The composition and analytical characters of French oil of lavender are discussed. Oil of *Tagetes anisata*, Lillo, which has an odour of anise, has d^{15} 0.9862, b. p. $214-218^{\circ}$, f. p. -6° , n_D 1.5432, $\alpha -1^{\circ} 10'$, saponification number, 3.1.

The table of structural formulæ, physical constants, and characteristic derivatives of essential oil constituents is continued.

CHEMICAL ABSTRACTS.

Oil of *Bystropogon Canus*. JULIA WHELAN (*J. Amer. Pharm. Assoc.*, 1922, 11, 337–338).—The total oil obtained by distillation in steam was 0.3%. The colour is green, somewhat like that of bergamot oil, and the odour more like that of fatty acid esters than of menthol; d^{20} 0.910; $[\alpha]_D -0.59^{\circ}$; n_D^{25} 1.563. Tests for pulegone, menthol, thymol, and carvacrol were negative.

CHEMICAL ABSTRACTS.

Essential Oil of the Leaves of *Doryphora sassafras*. A. R. PENFOLD (*Perf. Essent. Oil Rec.*, 1922, 13, 273–275).—The leaves of *Doryphora sassafras*, the New South Wales variety of the sassafras tree, yield, according to season, 0.1–1.05% of essential oil, the former quantity being obtained in May and the latter in November. The oil varies considerably in composition according to the districts from which it is obtained. Leaves from the Monga district gave an oil having the following constants: d 1.01–1.02; n 1.506–1.509; α $+16.2^{\circ}$ to $+22.2^{\circ}$; ester value, 4.6 (after acetylation, 32.97); solubility in 70% alcohol, 1 in 8. The principal constituents so far identified are safrole, 60–65%; camphor, 10–15%; *d*- α -pinene, 10%; sesquiterpenes, 10%; eugenol, 1%. Another sample of oil from the Currowan district was lighter than water (d 0.9808) and contained about 30% only of safrole, together with a considerable quantity of a substance which was apparently eugenol methyl ether, but which has not yet been satisfactorily separated from admixed sesquiterpenes and alcoholic substances.

The proportion of camphor in this oil was also greater, amounting to about 30%.
G. F. M.

The Volatile Oil of *Mentha aquatica*, Linné, and a Note on the Occurrence of Pulegone. ROLAND E. KREMER (J. Biol. Chem., 1922, 52, 439—443).—The distilled oil of *Mentha aquatica*, Linné, has d_{20}^{25} 0.916; n_D^{25} 1.4582; $[\alpha]_D^{25}$ -7.48° ; acid number, 7.84; ester number, 210.93; ester number after acetylation, 224.0; and contains 73.82% of ester, 61.6% of total alcohol, 3.6% of free alcohol. The ester consists mainly of linalool acetate. There are also present small quantities of another ester, free linalool, a free acid, and an unstable aldehyde.

Pulegone is a constituent of the cohobated oil of peppermint (cf. this vol., i, 357).
E. S.

Essential Oil of Violet Roots. A. GORIS and CH. VISCHNAC (Bull. Sci. Ind. Roure-Bertrand Fils, 1921, [iv], 3, 1—8; from Chem. Zentr., 1922, i, 360).—The roots of violet (*Viola odorata*) contain an essential oil and a glucoside. The ethereal oil is a salicylic ester. The amount of glucoside is small. It is acted on by an enzyme contained in the root with the formation of an essential oil of strong odour.
G. W. R.

The Vulcanisation of Caoutchouc in Solution. F. BOIRY (Compt. rend., 1922, 175, 102—104).—If caoutchouc is heated, in colloidal solution, with sulphur at 120° the product depends on the concentration of the solution and the nature of the solvent. With dilute solutions (1—2%), and with solvents such as nitrobenzene, petrol, phenetole, etc., a gelatinous deposit is obtained which, when dried, is a hard, elastic mass with a black fracture. After extraction with acetone, it contains 15—30% of "combined" sulphur. With solvents such as aniline, xylene, thymol, etc., no precipitate is obtained even after several weeks' boiling. With 10% solutions in solvents of the first group, the viscosity of the solution at first diminishes on heating, then reaches a minimum, and increases rapidly until the liquid forms a gel. These gels show the phenomenon of syneresis. The sulphur content of the products obtained, after extracting the gels with acetone, varies between 20 and 30%.
W. G.

The Glucosides. I. The Constitution of Indican. ALEXANDER KILLEN MACBETH and JOHN PRYDE (T., 1922, 121, 1660—1668).

Digitonin and its Derivatives. A. WINDAUS and K. WEIL (Z. physiol. Chem., 1922, 121, 62—79; cf. Kiliani, A., 1890, i, 996; 1891, i, 576; 1919, i, 90).—Digitonin has the formula $C_{55}H_{90}O_{28}$. On hydrolysis by alkali, the products are (i) digitogenin, $C_{26}H_{42}O_5$, a neutral material containing three hydroxyl groups, and forming a triacetyl derivative, $C_{36}H_{50}O_5Ac_3$, needles, m. p. 190° , (ii) a hexose, (iii) a pentose, according to the equation $C_{55}H_{90}O_{28} + 5H_2O = C_{26}H_{42}O_5 + 4C_6H_{12}O_6 + C_5H_{10}O_5$. Digitogenin, which does not possess lactone, methoxyl, aldehyde, or ketone groups, is oxidised

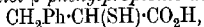
by chromic acid to digitogenic acid, which is now shown to have the formula $C_{26}H_{38}O_7$, to yield a dimethyl ester, $C_{28}H_{36}O_7Me_2$, m. p. 146° , and a diethyl ester, $C_{28}H_{36}O_7Et_2$. Citonic acid, deoxydigitogenic acid, and hydrodigitoic acid, described by Kiliani, are all really impure forms of digitogenic acid. Digitoic acid and β -digitogenic acid, isomeric with digitogenic acid, from which they are formed on warming with alkali, both yield the same dimethyl ester, $C_{28}H_{42}O_7$, m. p. 140° . On boiling with potassium hydroxide solution, the dimethyl esters of digitoic acid, digitogenic acid, and β -digitogenic acid all yield digitoic acid. Oxydigitogenic acid, from the oxidation of digitoic acid, digitogenic acid, or β -digitogenic acid, has the formula $C_{26}H_{38}O_9$ (trimethyl ester, $C_{29}H_{44}O_9$, m. p. 153°). It loses carbon dioxide easily on boiling with acetic acid and some mineral acid, indicating a β -ketonic acid or a derivative of malonic acid. Further oxidation yields digitic acid, $C_{26}H_{38}O_{10}$ (dimethyl ester, $C_{29}H_{44}O_{10}$, m. p. 137 – 138°). This ester differs from the previously described esters in that it contains a hydroxyl group. On treatment with acetic acid and hydrogen chloride at 0° , it loses 1 molecule each of carbon dioxide and of water to form anhydrodigitic acid, which presumably has the formula $C_{25}H_{36}O_7$. W. O. K.

Hyssopin. O. A. OESTERLE (*Schweiz. Apoth. Ztg.*, 1921, 59, 548—553; from *Chem. Zentr.*, 1922, i, 579).—*Hyssopin*, $C_{50}H_{66}O_{30} \cdot 3H_2O$, which occurs as crystals in hyssop plants attacked by fungi, is a rhamnoglucoside similar to hesperidin; it forms spherulitic crystals, m. p. 275 – 276° . *Hyssopinglycone*, $C_{16}H_{14}O_6$, forms bright ochre-yellow platelets, m. p. 262 – 263° . *Hyssopinglycone acetate*, $C_{16}H_{11}O_6Ac_3$ or $C_{16}H_{10}O_6Ac_4$, forms white needles.

G. W. R.

The Use of Rhodanine in Organic Syntheses. I. Furfuralaniline. CH. GRÄNACHER (*Helv. Chim. Acta*, 1922, 5, 610—624).—The condensation products of rhodanine with aldehydes are readily decomposed by alkalis, and a study of their decomposition has shown that by this means many organic compounds not otherwise readily accessible may be synthesised. It has been previously observed by several authors that the condensation product of rhodanine with benzaldehyde breaks up, forming α -thioleinnamic acid. This reaction is found to occur readily on warming with 10–15% sodium hydroxide solution. α -Thioleinnamic acid is found to behave in many respects as the α -thio-keto-carboxylic acid, $CH_3Ph \cdot CS \cdot CO_2H$, and is therefore to be considered a tautomeric substance. It gives phenylpyruvic acid oxime, which melts with decomposition at 173 – 174° , not at 159 – 160° , as has been stated. It also reacts with other amines, giving derivatives of pyruvic acid with loss of sulphur. The oxime can be readily hydrolysed to pyruvic acid or reduced to an α -amino-acid. It is thus possible to pass from benzaldehyde directly to pyruvic acid or phenylalanine, and in the same way from furfuraldehyde to furfuralaniline. The α -thio-ketonic acids may also be converted into the α -ketonic acids by simply boiling with ammonia.

The oxime can also be reduced to give a nitrile containing one carbon atom more than the original aldehyde. Further, α -thiolcinnamic acid can be reduced to β -phenylpropionic acid, a saturated acid containing two carbon atoms more than the original aldehyde. By reduction of α -thioleinnamic acid in alkaline solution with sodium amalgam, α -thiol- β -phenylpropionic acid,



was obtained. It forms a thick syrup with an unpleasant odour, cannot be distilled, and gives with ferric chloride and a trace of ammonia a fugitive blue coloration.

α -Thiol- β -2-furylacrylic acid (Andreasch, A., 1919, i, 97) forms with hydroxylamine α -oximino- β -2-furylpyruvic acid, white needles, m. p. 145°. By reduction with sodium amalgam in alcohol in presence of lactic acid to give the necessary acidity, this is reduced to 2-furylalanine, a coarse, crystalline powder decomposing at 252°. With phenylcarbimide in alkaline solution, this is condensed to α -phenylcarbimido- β -2-furylpropionic acid, m. p. 177–178°, not 162–163° as given by Sasaki (A., 1921, i, 808). E. H. R.

A Synthesis of Pyrylium Salts of Anthocyanidin Type. DAVID DOIG PRATT and ROBERT ROBINSON (T., 1922, 121, 1577–1585).

The Coumaranone Series. II. The Preparation of 4- and 6-Chlorocoumaran-2-ones and their Conversion into 2- and 4-Chloroflavonols respectively, and some Derivatives of o- and p-Chlorophenoxyacetic Acids. THOMAS HOSKER MINTON and HENRY STEPHEN (T., 1922, 121, 1598–1603).

The Thiophen Series. XIII. The Action of Acetylene on Pyrites. WILHELM STEINKOPF and JULIUS HEROLD (*Annalen*, 1922, 428, 123–153; cf. A., 1914, i, 425).—The product of the action of acetylene on finely divided pyrites at 300° contains the following substances: carbon, hydrogen, carbon disulphide, methane, butadiene, acetaldehyde, hydrogen sulphide, acetone, benzene, thiophen (about 40%), 2-thiotolen, 3-thiotolen, 2:3-thioxen, 2-ethylthiophen, and 3-ethylthiophen, and probably, in addition, butane, Δ^2 -butinene, toluene, and xylene, as well as higher homologues of acetylene.

The thiophen homologues were identified for the most part by means of their mercury compounds, many of which had previously been prepared from synthetic specimens of the alkylthiophens (A., 1921, i, 630). 2- and 3-Ethylthiophen, however, had not been fully characterised previously and the following facts relating to these substances had to be ascertained in order to establish their presence in the mixture.

3-Ethylthiophen, on treatment with mercuric chloride, yields 3-ethylthiophen-2(or 5)-mercurichloride, which forms colourless crystals, m. p. 67–68°, and 3-ethylthiophen-2:5-dimercurichloride, microscopic, filamental needles, m. p. 295–297° (decomp.). The former, on treatment with 2 molecules of sodium thiocyanate, gives mercury 3:3'-diethyldithienyl, needles, m. p. 68°, but no mercurithiocyanate.

2-Ethyl-5-thienyl methyl ketone, prepared from 2-ethylthiophen by the phosphoric oxide method (A., 1921, i, 579), gives a *semi-carbazone* which crystallises from alcohol in leaflets, m. p. 215°, with previous sintering. C. K. I.

Thiophen Series. XIV. The Condensation of Diazoacetic Ester with Thiophen. WILHELM STEINKOFF and HALVARD AUGESTAD-JENSEN (*Annalen*, 1922, 428, 154—163).—Condensation between ethyl diazoacetate and thiophen takes place at 127°, giving a poor yield of an ester, b. p. 113·5—114·5°/13 mm., which is believed to be *ethyl dicyclo-Δ²-α-penthiophen-5-carboxylate*, $\begin{array}{c} \text{CH} - \text{CH} \\ | \quad | \\ \text{CH} \cdot \text{S} \cdot \text{CH} \end{array} > \text{CH} \cdot \text{CO}_2\text{Et}$, rather than any of the possible monocyclic

isomerides, because the ease with which it forms an *amide*, long needles, m. p. 165°, on treatment with ammonia, suggests that the carbethoxy-group is not attached to a quaternary carbon atom. Both the ester and the amide yield an *acid*, $\text{C}_8\text{H}_6\text{O}_2\text{S}$, on hydrolysis with sodium hydroxide, but, as it is not clear whether or no isomerisation occurs during hydrolysis, a definite structure is not assigned to this substance. C. K. I.

Preparation of the Alkaloidal Mercuri-iodides in Crystalline Form. MAURICE FRANÇOIS and LOUIS GASTON BLANC (*Compt. rend.*, 1922, 175, 169—171).—The amorphous precipitate obtained by adding potassium mercuric iodide to a solution of an alkaloidal salt can be brought into solution by warming it in suspension in the mother-liquor with a large excess of hydrochloric acid, and on allowing to cool slowly it is usually redeposited in a crystalline form. In the actual preparation of these crystals the initial precipitation may be avoided by slowly mixing equal volumes of warm solutions of the alkaloidal salt containing a large amount of hydrochloric acid, and of potassium mercuric iodide, of suitable concentrations. Clear solutions are thus obtained from which the alkaloidal mercuri-iodides are deposited in crystals on slowly cooling. In this way, the mercuri-iodides of caffeine, theobromine, quinine, morphine, codeine, cocaine, strychnine, pilocarpine, and sparteine, and also of quinoline, were prepared. They form brilliant yellow crystals, containing neither chlorine nor water of crystallisation. They show a tendency, well marked in the case of the caffeine compound but scarcely perceptible with the less soluble compounds such as that of quinine, to be decomposed by water into mercuric iodide and the alkaloidal hydriodide.

G. F. M.

Preparation of the Alkaloidal Bismuthic Iodides in a Crystalline Form. MAURICE FRANÇOIS and LOUIS GASTON BLANC (*Compt. rend.*, 1922, 175, 273—274).—Crystalline bismuthic iodides of caffeine, theobromine, morphine, codeine, quinine, atropine, arecoline, pilocarpine, sparteine, nicotine, aniline, pyridine, and quinoline were prepared from potassium bismuthic iodide and acid solutions of the hydrochlorides of the bases by methods precisely analogous to those employed for the preparation of the

double mercuric iodides (preceding abstract). These compounds form extremely well-defined microscopic crystals, and in the bulk are considerably darker in colour than the corresponding amorphous substances. They contain no water of crystallisation, and have the general formula $(\text{BI}_3)_x(\text{AlkHI})_y$. They appear to be adapted for the microchemical characterisation of the alkaloids.

G. F. M.

Anhalonium Alkaloids. IV. Synthesis of Anhalamine. ERNST SPÄTH and HANS RÖDER (*Monatsh.*, 1922, 43, 93—111).—6-Hydroxy-7:8-dimethoxy-1:2:3:4-tetrahydroisoquinoline has been prepared synthetically, and shown to be identical with anhalamine.

At the outset it was supposed that anhalamine might be 7-hydroxy-6:8-dimethoxy-1:2:3:4-tetrahydroisoquinoline, and therefore this substance was synthesised. It was necessary, in the first place, to prepare β -4-ethylcarbonato-3:5-dimethoxyphenylethylamine, and two methods were attempted. The starting point of the first was carbethoxysinapic acid (4-ethylcarbonato-3:5-dimethoxycinnamic acid), which was reduced by hydrogen in the presence of palladium and platinum to carbethoxydihydrosinapic acid (β -4-ethylcarbonato-3:5-dimethoxyphenylpropionic acid), m. p. 167—169°. The same end-product was obtained by reducing carbethoxysyringylidenemalonic acid (4-ethylcarbonato-3:5-dimethoxybenzylidenemalonic acid) under similar conditions to 4-ethylcarbonato-3:5-dimethoxybenzylmalonic acid, m. p. 122—123° (decomp.), and effecting the elimination of a carboxyl group from this substance by heating. The carbethoxydihydrosinapic acid was converted into its *chloride*, and thence into its *amide*, m. p. 122—123°, from which it was hoped to obtain the required ethylamine by the action of bromine and alkali. The sole isolable product, however, was β -4-hydroxy-3:5-dimethoxyphenylpropionamide, m. p. 153—154°, hydrolysis of the carbonato-group having taken place.

Carbethoxysyringaldehyde (4-ethylcarbonato-3:5-dimethoxybenzaldehyde) was therefore condensed with nitromethane to give ω -nitro-4-ethylcarbonato-3:5-dimethoxystyrene, yellow crystals, m. p. 167°, which was reduced by zinc dust and acetic acid to 4-ethylcarbonato-3:5-dimethoxyphenylacetaldoxime. This was reduced, without purification, by means of sodium amalgam to β -4-ethylcarbonato-3:5-dimethoxyphenylethylamine, an oil which gave a crystalline *hydrochloride*, *platinichloride*, and *picrate*, m. p. 200° (decomp.).

The base was now condensed with formaldehyde to give 7-ethylcarbonato-6:8-dimethoxy-1:2:3:4-tetrahydroisoquinoline. This base gave a crystalline *hydrochloride*; on removal of the carbethoxy-group and methylation by means of methyl sulphate and alkali, it yielded 6:7:8-trimethoxy-2-methyl-1:2:3:4-tetrahydroisoquinoline methiodide, and on hydrolysis it gave 7-hydroxy-6:8-dimethoxy-1:2:3:4-tetrahydroisoquinoline, m. p. 166—167°, which was different from anhalamine.

A similar series of experiments was therefore instituted with

the isomeric aldehyde, 5-ethylcarbonato-3:4-dimethoxybenzaldehyde, but, at the outset, difficulties were encountered in the preparation of this substance. 5-Nitroveratraldehyde was reduced to 5-aminoveratraldehyde, which was isolated as the tin double salt and diazotised. The hydrolysis product of the diazonium salt was not 5-hydroxyveratraldehyde, however, but 4:5-dihydroxy-3-methoxybenzaldehyde, a methyl group having been eliminated. Methylation of this gave 3:4:5-trimethoxybenzaldehyde, so that this way to the desired substance appeared to be closed. The methylation of gallic acid was therefore investigated. Methyl sulphate gave a mixture of methyl 4:5-dihydroxy-3-methoxybenzoate, methyl 5-hydroxy-3:4-dimethoxybenzoate, and methyl 3:4:5-trimethoxybenzoate, and by further methylation of the first of these a mixture of the second and third could be obtained. The methyl 5-hydroxy-3:4-dimethoxybenzoate was hydrolysed with alkali to 5-hydroxy-3:4-dimethoxybenzoic acid, which was condensed with ethyl chlorocarbonate to give 5-ethylcarbonato-3:4-dimethoxybenzoic acid, m. p. 117–118°. This substance was converted into its chloride, m. p. 45–46°, by means of phosphorus pentachloride, and the chloride reduced by hydrogen to 5-ethylcarbonato-3:4-dimethoxybenzaldehyde, m. p. 60–60·5°. This on hydrolysis gave 5-hydroxy-3:4-dimethoxybenzaldehyde, m. p. 62–63°.

The carbonato-aldehyde was now condensed with nitromethane to give *o*-nitro-5-ethylcarbonato-3:4-dimethoxystyrene, m. p. 96°, which on reduction gave β -5-hydroxy-3:4-dimethoxyphenylethylamine, a brown, amorphous mass. This yielded anhalamine on condensation with formaldehyde.

As the yield in this last condensation was not good, the method was modified. 5-Hydroxy-3:4-dimethoxybenzoic acid was benzylated, but the 5-benzoyloxy-3:4-dimethoxybenzoic acid so obtained, m. p. 170–172°, could not be reduced to the aldehyde. 5-Hydroxy-3:4-dimethoxybenzaldehyde was therefore directly benzylated. 5-Benzoyloxy-3:4-dimethoxybenzaldehyde, m. p. 54°, on condensation with nitromethane, gave *o*-nitro-5-benzoyloxy-3:4-dimethoxystyrene, m. p. 104–105°, which, on reduction, yielded β -5-benzoyloxy-3:4-dimethoxyphenylethylamine (picrate, m. p. 163°). This, on condensation with formaldehyde and subsequent digestion with hydrochloric acid (to remove the benzyl group), gave anhalamine.

C. K. I.

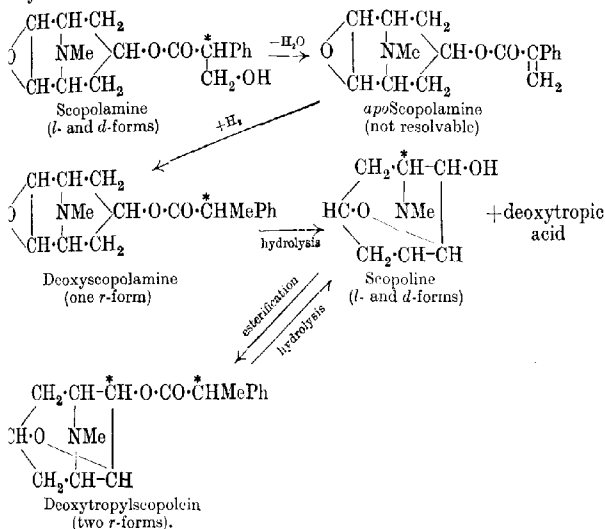
Preparation of Amino-derivatives of Hydrogenated Cinchona Alkaloids and their Derivatives. HOWARD & SONS, LTD., JOHN WILLIAM BLAGDEN, and MAXIMILIAN NIERENSTEIN (Brit. Pat. 182986).—Good yields of the amino-derivatives of hydrogenated cinchona alkaloids are obtained by reducing the nitro-derivatives in neutral or nearly neutral solution with suitable reducing agents such as zinc or iron in conjunction with a neutral salt. Thus nitrohydroquinine, dissolved in alcohol, or in water in the form of a salt, is heated at 50° or more, and zinc dust and aqueous ammonium sulphate solution are added. After stirring for some hours at this temperature, the filtered solution is concentrated in a vacuum to crystallise the product. G. F. M.

Preparation of Morphine Allyl Ether. GEORG VON KERESZTY and EMIL WOLF (D.R.-P. 343055; from *Chem. Zentr.*, 1922, ii, 147).—A solution of an alkali metal compound of morphine is allowed to react with an alcoholic solution of an allyl arylsulphonate. By the action of sodium morphine on allyl benzènesulphonate, *allyl morphine ether* is obtained; it forms a *hydrochloride* ($+1\text{H}_2\text{O}$), which has m. p. 129–131° when heated quickly, or 130–132° if heated slowly. The free base has m. p. 67–68°. It has therapeutic uses.

G. W. R.

Scopoline. VI. The Constitutions of Scopolamine and Scopoline. The Hofmann Degradation of Scopoline. KURT HESS and OTTMAR WAHL (*Ber.*, 1922, 55, [B], 1979–2025).—Inactive scopoline, obtained by the hydrolysis of *l*-scopolamine with acids or alkalis, has been shown by King (T., 1919, 115, 476, 974; cf. Tutin, T., 1910, 97, 1793) to be a racemic form of *d*- and *l*-scopoline and, since the active scopolines are not racemised under such conditions as are used in the hydrolysis of scopolamine, he has drawn the conclusion that *r*-scopoline is present initially in *l*-scopolamine and that the optically asymmetric character of the latter is due to the presence of the optically active tropyl group. The conception of *l*-scopolamine as a partial racemate appears to the authors improbable on theoretical grounds, and also on account of the non-observation of a transition temperature for *l*-scopolamine and the failure of attempts to resolve *dl*-*aposcopolamine*. More conclusive evidence has been sought by attempts to synthesise *l*-scopolamine from *dl*-scopoline and *l*-tropic acid, the initial experiments being conducted with optically inactive material. Direct attempts were unsuccessful by reason of the reactivity of the hydroxyl group of tropic acid, whilst acetyltropyl bromide and scopoline gave acetylscopoline. Esterification of *dl*-scopoline with atropic acid was rendered impossible by reason of the polymerisation of the latter. Greater success was encountered with deoxytropic (α -phenylpropionic) acid. From the *r*-acid and *dl*-scopoline, two racemic products are derived, whereas, according to King's conception, the formation of a single partial racemate is more probable. It must therefore be assumed that either this conception is incorrect or that the ester differs in its behaviour from scopolamine and *aposcopolamine*. If the latter hypothesis is correct, the compound derived from the partly racemic scopolamine by hydrogenation of the corresponding *apo*-derivative must be a separable mixture of racemates which are identical with the compounds just described. Experiment, however, shows that the deoxyscopolamine which is prepared readily from *aposcopolamine* is a single racemic form which is not identical with either of the products derived from scopoline and deoxytropic acid. Since the acid component of the three esters is the same, the difference must be caused by the alcoholic component; hence the alcoholic component of deoxyscopolamine, and therefore of scopolamine itself, cannot be identical with scopoline. It follows also that only one asymmetric carbon atom is present in deoxy-

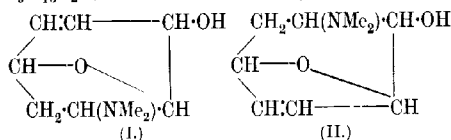
scopolamine, and hence in scopolamine; since this is located in the tropanyl residue, a symmetrical structure must be assigned to the basic portion of scopolamine. As, however, an asymmetric carbon atom has been proved to be present in scopoline, it must be assumed that it is developed during the hydrolysis, which thus causes a structural change in the basic component of scopolamine. Further confirmation of this hypothesis is derived from the observation that the three isomeric deoxyscopolamines and the two racemates of deoxytropylscopolein yield the same products (scopoline and deoxytropic acid) when hydrolysed. The constitution assigned previously to scopolamine and its derivatives therefore requires revision; the reactions are interpreted satisfactorily by the following formulæ:—



Deoxytropic acid is prepared conveniently by the hydrogenation of atropic acid in glacial acetic acid solution in the presence of platinum and is converted by thionyl bromide (obtained by saturating boiling thionyl chloride with hydrogen bromide) into *deoxytropyl bromide*, a pale yellow liquid, b. p. 106–107°/13 mm. The latter reacts with scopoline hydrobromide in the presence of xylene at 140° with the formation of α - and β -deoxytropylscopolein bromides in approximately equal amount, which can be separated from one another mechanically or by seeding the solution of the mixture with one variety. α -Deoxytropylscopolein crystallises in large, thick rhombohedra, m. p. 66–67° (the *hydrobromide*, aggregates of needles, m. p. 205°; *picrate*, quadratic leaflets, m. p. 172°; *methiodide*, m. p. 195°, and *platinichloride*, yellow crystals, decomp.

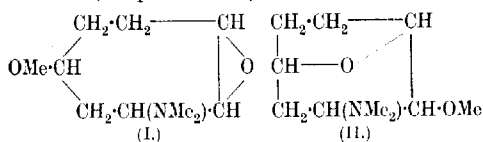
155—157°, are described). β -*Deoxytropylscopolin* forms large prisms, m. p. 63—64° [the *hydrobromide*, m. p. 176—177°; *picrate*, small cubes, m. p. 130°; *methiodide*, long, slender needles, m. p. 183°; *platinichloride*, m. p. 215° (decomp.), and oily *aurichloride* are described]. *apoScopolamine* is converted by hydrogen in the presence of spongy platinum and glacial acetic acid into *deoxy-scopolamine*, long, slender needles, m. p. 69°; the *hydrobromide*, m. p. 182—183°; *picrate*, thin leaflets, m. p. 209—210°; *methiodide*, leaflets, m. p. 219° (decomp.), and *platinichloride*, m. p. 220°, were analysed.

The new conception of the constitution of scopolamine permits a more definite hypothesis with regard to the Hofmann degradation of scopoline (cf. Hess, A., 1921, i, 683; Gadamer and Hammer, A., 1921, i, 588). The process has been shown to give rise to products which contain two double bonds but, under definite conditions which are now described, it can be so regulated that only compounds containing one double bond are formed. The product of the reaction consists of a mixture of four isomeric bases, $C_9H_{15}O_2N$, from which α -demethylscopoline (annexed formula I or



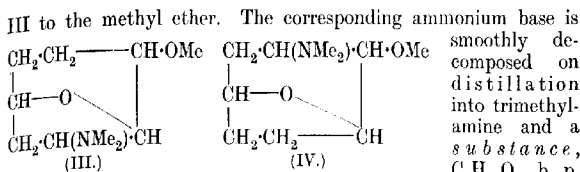
II) separates on cooling; the product is identical with that described previously as α - ψ -demethyl-

scopoline. The remaining bases are only separable from one another after hydrogenation. Under these conditions α -demethylscopoline gives α -*dihydrodemethylscopoline*, colourless, lustrous needles, m. p. 53° (the *picrate*, m. p. 183°, and *methiodide*, m. p. 209—210°, have been prepared previously from non-homogeneous material; the *benzoyl* compound has m. p. 219°). Distillation of the quaternary ammonium base of α -*dihydrodemethylscopoline* leads to the formation of *O-methyliso- α -dihydrodemethylscopoline*, b. p. 116—120°/13 mm. (*picrate*, rhombic crystals, m. p. 185°; *methiodide*, m. p. 240—241°), for which the annexed formulae I and



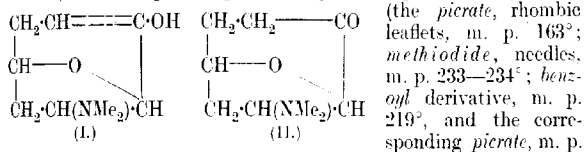
II are possible. The second formula is, however, practically excluded

by the following series of observations. α -*Dihydrodemethylscopoline* is converted by thionyl chloride into α -*dihydrodemethylscopoline chloride*, b. p. 115—118°/13 mm., m. p. 45° [*picrate*, m. p. 228° (decomp.)], which is transformed by sodium methoxide into the *methyl ether* of α -*dihydrodemethylscopoline*, b. p. 110—115°/14 mm. (*methiodide*, m. p. 174—175°). (α -*Dihydrodemethylscopoline* is unaffected by sodium methoxide under the experimental conditions adopted.) It therefore appears valid to assign the formula



70—71°/13 mm. In a similar manner, β -dihydrodemethylscopoline (see later) is converted successively into β -dihydrodemethylscopoline chloride, b. p. 122—125°/13 mm., m. p. 38—39°, and the methyl ether of β -dihydrodemethylscopoline (formula IV) (methiodide, lustrous leaflets, m. p. 225.5°). The degradation of the ammonium base of the latter gives trimethylamine and a nitrogen-free product, b. p. about 80°/15 mm. The smooth Hofmann degradation of these substances is in such striking contrast to the stability of *O*-methyliso- α -dihydrodemethylscopoline under similar conditions that the substances cannot be constituted similarly.

The liquid residue obtained after the removal of α -demethylscopoline is submitted to hydrogenation and the dihydro-products are separated by fractional crystallisation of the corresponding picrates. The following substances are thereby obtained: β -Dihydrodemethylscopoline, colourless, lustrous needles, m. p. 78°, b. p. 128—131°/13 mm. (picrate, large cubes, m. p. 153°; methiodide, rectangular leaflets, m. p. 249°); γ -Dihydrodemethylscopoline, b. p. 120—123°/13 mm. (picrate, large crystals, m. p. 194°; methiodide, m. p. 171°); demethylscopolinone (annexed formula I or II), lustrous, pointed prisms, m. p. 42°, b. p. 117—119°/13 mm.



213—214°, are described; the compound does not react with hydroxylamine or hydrazine hydrate).

α -, β -, and γ -Dihydrodemethylscopolines are reduced with comparative readiness by hydriodic acid and phosphorus to the amine, $\text{C}_8\text{H}_{17}\text{N}$, b. p. 59°/17 mm., 170—172°/756 mm. (picrate, needles, 157—158°), which contains two atoms of hydrogen less than the expected dimethylsuberylamine.

H. W.

Cevadine. I. ALEXANDER KILLEN MACBETH and ROBERT ROBINSON (T., 1922, 121, 1571—1577).

Derivatives of Pyrrole. WILLIAM KÜSTER [with W. WEBER, H. MAURER, W. NIEMANN, P. SCHLACK, SCHLAYERBACH, and WILIG] (Z. physiol. Chem., 1922, 121, 135—163).—By the reduction of a mixture of methyl acetoacetate and methyl oximinooctoacetate, methyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate,

needles, m. p. 174—175°, is obtained. From methyl acetoacetate and ethyl oximinoacetoacetate is obtained 3-ethyl 5-methyl 2:4-dimethylpyrrole-3:5-dicarboxylate, colourless needles, m. p. 158°, and in an analogous way, the 3-methyl 5-ethyl ester, colourless needles, m. p. 119—120°, can be prepared. On partial hydrolysis, these give respectively 2:4-dimethylpyrrole-3:5-dicarboxylic acid 3-ethyl ester, colourless needles, m. p. 202° (decomp.), and 2:4-dimethylpyrrole-3:5-dicarboxylic acid 3-methyl ester, colourless needles, m. p. 182° (decomp.). 2:4-Dimethylpyrrole-3:5-dicarboxylic acid 3-ethyl ester, when boiled with acetic anhydride, yields ethyl 2:4:2':4'-tetramethylpyrrocoll-3:3'-dicarboxylate, colourless needles, m. p. 257—258°, and over a free flame it loses carbon dioxide to form methyl 2:4-dimethylpyrrole-3-carboxylate. This and the analogous ethyl 2:4-dimethylpyrrole-3-carboxylate, when coupled with diazobenzenesulphonic acid, yield respectively methyl and ethyl 5-sulphobenzeneazo-2:4-dimethylpyrrole-3-carboxylate as red powders, unstable in the air. Ethyl 2:4-dimethylpyrrole-3-carboxylate condenses with formaldehyde, *m*-nitrobenzaldehyde, and furfuraldehyde to give bis(3-carbethoxy-2:4-dimethylpyrrol)-methane, bis(3-carbethoxy-2:4-dimethylpyrrol)-*m*-nitrophenylmethane, colourless needles, m. p. 180°, and bis(3-carbethoxy-2:4-dimethylpyrrol)-furylmethane, colourless needles, m. p. 176°. The first of these compounds on oxidation with chloranil yields bis(3-carbethoxy-2:4-dimethylpyrrol)-methene hydrochloride, a red dye, m. p. 215°. Bis(3-carbethoxy-2:4-dimethylpyrrol)-furylmethane, colourless needles, m. p. 198°, has also been prepared. Ethyl 3-hydroxy-5-methylpyrrole-4-carboxylate yields the following compounds: with anisaldehyde in presence of potassium hydrogen sulphate, 3-hydroxy-4-carbethoxy-5-methylpyrrolenyl-3-*p*-methoxyphenylmethane, yellow needles, m. p. 210°; with *p*-dimethylaminobenzaldehyde, 3-hydroxy-4-carbethoxy-5-methylpyrrolenyl-3-*p*-dimethylaminophenylmethane, red crystals; with furfuraldehyde, 3-hydroxy-4-carbethoxy-5-methylpyrrolenyl-3-furylmethane, yellow needles, m. p. 117° (decomp.); with acetone, in presence of sodium hydroxide and acetyl chloride, ethyl 3-hydroxy-5-methyl-2-isopropylidenepyrrolenine-4-carboxylate, short, pale yellow needles, which slowly decompose at 180—200°; with acetic anhydride and potassium acetate, ethyl 3-acetoxy-5-methylpyrrole-4-carboxylate, m. p. 120°; with acetic anhydride and sulphuric acid, ethyl 3-acetoxy-2-acetyl-5-methylpyrrole-4-carboxylate, light yellow needles, m. p. 167°, which on hydrolysis with alcoholic sodium ethoxide yields ethyl 3-hydroxy-2-acetyl-5-methylpyrrole-4-carboxylate, colourless, fine needles, m. p. 199° (semicarbazone, C₁₁H₁₆O₃N₄). 5-Acetyl-2:4-dimethylpyrrole forms a nitroso-derivative, small, deep green needles, m. p. 148—149°, and it couples with diazobenzenesulphonic acid to yield 5-acetyl-2:4-dimethylpyrrole-3-azobenzenesulphonic acid, greenish-black needles. Similarly, with diazonaphthalenesulphonic acid is obtained 5-acetyl-2:4-dimethylpyrrole-3-azonaphthalenesulphonic acid, dark blue, six-sided leaflets, which decompose at 210—212°. From methyl acetonedicarboxylate, acetic acid, sodium nitrite, and zinc dust is obtained methyl pyrrole-

3:5-diacetate-2:4-dicarboxylate, tufted crystals, m. p. 98—99°, which on partial hydrolysis yields a dibasic acid, $C_{12}H_{18}O_8N$.
W. O. K.

Complex Magnesium Salts. G. SPACU (*Bull. Soc. Ştiinţe Cluj*, 1921, 1, 72—91; from *Chem. Zentr.*, 1922, i, 313—314).—A number of complex pyridine compounds of magnesium containing combined water are described. *Tetra-aquodipyridine-magnesium chloride*, $[MgPy_2(H_2O)_4]Cl_2$, is obtained by the action of anhydrous pyridine on carnallite; it crystallises in colourless needles which deliquesce on exposure to air with liberation of pyridine. It gives magnesium hydroxide on treatment with ammonia, and silver chloride with silver nitrate. *Triaquotripyridine-magnesium chloride*, $[MgPy_3(H_2O)_3]Cl_2 \cdot H_2O$, is similar to the preceding compound. *Diaquotetrapyridinemagnesium bromide*,
 $[MgPy_4(H_2O)_2]Br_2 \cdot 2H_2O$,

forms very hygroscopic crystals which give up their water of crystallisation in a vacuum over phosphoric oxide. *Aquopentapyridinemagnesium iodide*, $[MgPy_5H_2O]I_2 \cdot 2H_2O$, forms crystals from which iodine separates on exposure to air; it is less hygroscopic than the preceding compounds: *Tetra-aquodipyridinemagnesium nitrate*, $[MgPy_2(H_2O)_4](NO_3)_2 \cdot 2H_2O$, forms nacreous lamellæ. The anhydrous salt has similar properties. *Hexapyridinemagnesium bromide*, $[MgPy_6]Br_2$, is prepared by the Tissier-Grignard reaction by way of the ether compound, $[MgPy_4(Et_2O)_2]Br_2$. The latter is a light yellow, unstable powder which gives with anhydrous pyridine at 100° the hexapyridinemagnesium bromide: the latter forms colourless platelets and is very hygroscopic and unstable. *Hexapyridinemagnesium iodide* is similarly prepared and resembles the corresponding bromide.

G. W. R.

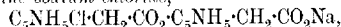
Complex Iridium Compounds. M. DELÉPINE (*Rev. gen. sci. pures appl.*, 1921, 32, 607—615; from *Chem. Zentr.*, 1922, i, 411).—A number of complex pyridine iridium compounds are described in connexion with a study of Werner's valency theory. *Potassium pentachloropyridineiridiate*, $K_2[Ir^{III}PyCl_5]$, is prepared from the corresponding aquo-salt or potassium iridichloride and pyridine at 100°. The alkali salts are reddish-brown, giving orange solutions; the silver and thallium salts are violet or blue. By chlorination of the above salt, *pentachloropyridineiridic acid*, $H[Ir^{IV}PyCl_5]$, is obtained: it is crystalline and gives a violet solution in amyl alcohol. *Potassium tetrachlorodipyridineiridiate*, $K[Ir^{III}Py_2Cl_4]$, is prepared similarly to the pentachloropyridine compound by longer heating. Two isomerides occur of orange-yellow and red colour respectively. The alkali, thallium, silver, and pyridine salts are similar. By oxidation with chlorine or nitric acid, *tetrachlorodipyridineiridium*, $Ir^{IV}Py_2Cl_4$, is obtained; it is crystalline, and with potassium iodide it gives potassium tetrachlorodipyridineiridiate and iodine. By the action of ammonia, a mixture of a compound, $[Ir^{III}Py_2(NH_3)_2Cl_2]_2[Ir^{III}Py_2Cl_4]$, and a compound, $[Ir^{III}Py_2(NH_3)_3Cl][Ir^{III}Py_2Cl_4]_2$, is obtained. Tetra-chlorodipyridineiridium, prepared from orange-coloured salts,

shows green and reddish-violet dichroism in polarised light and is the *cis*-form, isomorphous with the corresponding platinum compound. *Potassium dioxalodipyridineiridate*, $K[Ir^{III}Py_2(C_2O_4)_2]$, is prepared from pyridine and potassium trioxaloiridate or potassium dichlorodioxaloiridate at 130° . It is crystalline and gives with hydrogen chloride at 130° a compound, $[Ir^{III}Py_2(H_2O)Cl(C_2O_4)]$, yellow needles, and a compound, $[Ir^{III}Py_2(H_2O)_2Cl_2][Ir^{III}Py_2Cl_4]$, orange-yellow prisms. The latter compound gives with ammonia, ammonium tetrachlorodipyridineiridate, $NH_4[Ir^{III}Py_2Cl_4]$, and a compound, $[Ir^{III}Py_2(H_2O)(OH)Cl_2]$, forming yellow crystals. The dioxalodipyridine compound cannot be resolved into optical isomerides. The *cis*-form of the compound, $K_3[Ir^{III}Cl_2(C_2O_4)_2]$, can be resolved into optically active constituents by way of the strychnine compounds. The *cis*-form is changed into the *trans*-form by heating at 130° . The *trans*-form is also obtained by way of potassium hexachloroiridate and potassium oxalate.

Trichlorotripyridineiridium, $[Ir^{III}Py_3Cl_3]$, is obtained from potassium tetrachlorodipyridineiridate by heating at 130° . From the orange-coloured modification two isomerides can be isolated, whilst from the red modification only one compound is obtainable. The orange-coloured salts and their products correspond throughout with the *cis*-form, and may give optical isomerides, whilst the red salts correspond with optically inactive *trans*-forms.

G. W. R.

Preparation of Compounds of Pyridinebetaine with Metallic Salts. LEOPOLD CASSELLA & Co., G. M. B. H. (D.R.P. 343148; from *Chem. Zentr.*, 1922, ii, 146).—By the action of metallic salts on pyridinebetaine in concentrated aqueous solution, compounds are obtained which serve as glycerol substitutes. *Dipyridinebetaine sodium chloride*,



is obtained by the action of sodium carbonate on dipyridinebetaine hydrochloride; it is a viscid liquid, d_{15}^{20} 1.26. *Dipyridinebetaine calcium chloride* has d_{15}^{20} 1.28. *Dipyridinebetaine potassium iodide* is a light yellow liquid, d_{15}^{20} 1.475. *Dipyridinebetaine mercuric chloride* forms long needles. *Dipyridinebetaine sodium salicylate* is also mentioned. The alkali and alkaline-earth metallic compounds are strongly hygroscopic and with the addition of small quantities of water form viscous liquids having many of the properties of glycerol. They may be crystallised by concentration and cooling.

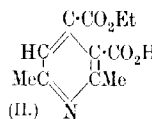
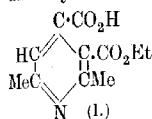
G. W. R.

Preparation of a Derivative of Pyridine-3-carboxylic Acid (Nicotinic Acid). SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 90807; from *Chem. Zentr.*, 1922, ii, 324–325).—Compounds containing a pyridine-3-carboxylic acid residue are treated with diethylamine. For example, the acid chloride is treated with diethylamine hydrochloride for two hours at 160° . From the product of the reaction, *pyridine-3-carboxyldiethylamide* is obtained as a yellow oil, b. p. $175^\circ/25$ mm. It has therapeutic uses.

G. W. R.

Preparation of Quaternary Ammonium Salts of Pyridine-3-carboxylic Acid Alkyl Esters. RICHARD WOLFFENSTEIN (D.R.P. 343054; from *Chem. Zentr.*, 1922, ii, 145—146).—Alkyl pyridine-3-carboxylates are treated with alkyl salts, excepting alkyl haloids. *Methyl 1-methylpyridine-3-carboxylate methosulphate*, obtained by the action of methyl sulphate on methyl pyridine-3-carboxylate, is a light yellow, uncrystallisable oil. The quaternary compound from the action of ethyl nitrate on *ethyl pyridine-3-carboxylate* is a thick, light brown oil. *Amyl pyridine-3-carboxylate* and methyl sulphate give similarly a quaternary compound, which is an almost colourless oil. G. W. R.

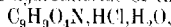
The Hydrogen Esters of 2:6-Dimethylcinchomeronic Acid. OTTO MUMM and ELSE GOTTSCHALDT (*Ber.*, 1922, 55, [B], 2064—2075).—In a previous communication, the ethyl hydrogen ester obtained by the partial hydrolysis of ethyl 2:6-dimethylcinchomeronate has been regarded as the 3-ester (I),



whereas that prepared by the action of ethyl alcohol on the acid anhydride has been considered to be the 4-compound (II), the formulæ assigned resting mainly on considerations of the possibility of steric hindrance (Mumm and Hüneke, A., 1918, i, 184). Since, however, Wegscheider (A., 1920, ii, 761) has more recently pointed out that such considerations are frequently not applicable to esters containing nitrogen, further confirmation appeared to be necessary. Conclusive evidence of the correctness of the previously assigned formulæ is now obtained by investigation of the behaviour of the synthetic methyl ethyl dimethylcinchomeronates.

3-Methyl 4-ethyl 2:6-dimethylcinchomeronate, b. p. 158°/13 mm., m. p. 22°, is prepared by the condensation of ethyl acetoneoxalate with methyl β-aminocrotonate; the corresponding *picrate* has m. p. 143—144°. Conversely, methyl acetoneoxalate and ethyl β-aminocrotonate give 4-methyl 3-ethyl 2:6-dimethylcinchomeronate, prisms, m. p. 52°, b. p. 115°/0.45 mm. (*picrate*, needles, m. p. 137°), whereas methyl β-aminocrotonate and methyl acetoneoxalate yield methyl 2:6-dimethylcinchomeronate, colourless needles, m. p. 48°.

3-Methyl 4-ethyl dimethylcinchomeronate is completely hydrolysed by boiling concentrated hydrochloric acid to dimethylcinchomeronic acid (the *hydrochloride* of the latter,



long prisms, which do not melt below 330°, is described). It is converted by the calculated quantity of potassium hydroxide in alcoholic solution into 3-methyl hydrogen dimethylcinchomeronate, needles, m. p. 198—199°. (4-Methyl hydrogen 2:6-dimethylcinchomeronate, colourless, rhombic plates, m. p. 165°, is prepared by the action of absolute methyl alcohol on 2:6-dimethylcinchomeronic anhydride.) Similarly, 4-methyl 3-ethyl 2:6-dimethyl-

cinchomerone is transformed by partial hydrolysis into 3-ethyl hydrogen 2:6-dimethylcinchomerone, slender needles, m. p. 165°, which is identical with the substance described previously (Mumm and Hüneke, *loc. cit.*).

3-Ethyl silver 2:6-dimethylcinchomerone is converted by distillation in a vacuum into ethyl dimethylnicotinate, b. p. 118°/18 mm. (picrate, m. p. 139°).

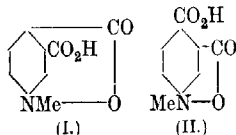
2:6-Dimethylcinchomeronic acid is transformed by ethyl alcohol and hydrogen chloride into 4-ethyl hydrogen 2:6-dimethylcinchomerone, m. p. 151–152°. The action of potassium methyl sulphate on potassium 2:6-dimethylcinchomerone at 135° gives the dimethyl ester, m. p. 48°.

The following data are recorded for the affinity constants: 2:6-dimethylcinchomeronic acid, 0.1666 (in about 0.01N-solution); 3-ethyl hydrogen ester, 0.0019; 4-ethyl hydrogen ester, 0.0021.

H. W.

Apophyllenic Acid and $\alpha\alpha'$ -Dimethylapophyllenic Acid.

OTTO MUMM and ELSE GOTTSCHALDT (*Ber.*, 1922, 55, [B], 2075–2082).—Apophyllenic acid was isolated by Wöhler (1844) as a product of the degradation of narcotine, and has subsequently been shown to have the constitution indicated by the annexed formula I or II. The authors have attempted to decide between the two alternatives in the following manner. Ethyl 2:6-dimethylcinchomerone is converted by successive treatment with methyl iodide and moist silver oxide into ethyl dimethylapophyllenate, from



which the corresponding free acid is readily obtained. If this reaction is applied to 3-methyl 4-ethyl 2:6-dimethylcinchomerone, ethyl dimethylapophyllenate (identical with the product derived from the diethyl ester) must be obtained if the compound is a 3-betaine, whereas if it is a 4-betaine it must yield methyl dimethylapophyllenate (identical with the substance derived from the dimethyl ester). The latter is, however, exclusively produced, so that free 2:6-dimethylapophyllenic acid must be regarded as a 4-betaine, and this, by analogy, is true also for apophyllenic acid itself. In each case the more powerfully acidic carboxyl group takes part in the internal salt formation. The conception of apophyllenic acid as a 4-betaine is in harmony with its properties, except that its silver salt is converted by methyl iodide into the 4-methyl ester of cinchomeronic acid 3-betaine. The apparent exception may possibly be explained on the basis of Pfeiffer's hypothesis (this vol., i, 720), according to which the betaines, like true salts, are completely ionised even in the solid state. The formation of the silver salt is therefore a purely ionic reaction, and it is immaterial whether it is a 3- or a 4-betaine, since either would give initially the same ion.

The following substances are described: Ethyl 2:6-dimethylcinchomerone methiodide, yellow needles, m. p. 139°; ethyl

2:6-dimethylapophyllenate, short, colourless needles (+H₂O), m. p. 112°, m. p. (anhydrous) 185°; methyl 2:6-dimethylcinchomeranate methiodide, slender, yellow needles, m. p. 188—189°; methyl dimethylapophyllenate (trihydrate and anhydrous), colourless needles, decomp. about 235° after darkening at 205°; 3-methyl 4-ethyl 2:6-dimethylcinchomeranate methiodide, slender matted needles, m. p. 169—170° (decomp.); 2:6-dimethylapophyllenic acid (monohydrate and anhydrous), slender needles, m. p. 237—238°.

H. W.

The Mechanism of the Fischer Indole Synthesis. CECIL HOLLINS (*J. Amer. Chem. Soc.*, 1922, **44**, 1598—1600).—The explanations of the Fischer synthesis advanced by Robinson and Robinson (T., 1918, **113**, 639), Cohn ("Die Carbazolgruppe," 1919, p. 12), Bamberger and Landau (A., 1919, i, 395), and Reddelien (A., 1912, i, 363) are criticised. The last-named appears to be the most satisfactory, and its apparent failure in the case of phenylmethylhydrazones disappears if the ketone imide is supposed to react in its tautomeric form: $\text{NH}\cdot\text{CR}\cdot\text{CH}_2\text{R} \rightleftharpoons \text{NH}_2\cdot\text{CR}\cdot\text{CHR} \xrightarrow{+\text{NMePh}} \text{NMePh}\cdot\text{CR}\cdot\text{CHR}$

$\xrightarrow{-\text{H}_2} \text{C}_6\text{H}_4\langle\text{CR}\rangle\text{CR}$. Thus modified, Reddelien's theory fulfils all the conditions required: (a) an indolenine is the primary product where this is possible; (b) isobutyraldehyde and ketones of the type $\text{CHMe}_2\cdot\text{CO}\cdot\text{R}$ are converted into indolenines with extraordinary ease (due to the ready oxidisability of the CHMe_2 group); (c) the reaction succeeds with phenylmethylhydrazones; (d) the tertiary nitrogen atom, that is, that remote from the benzene nucleus, is the one removed; (e) acid hydrazides undergo a similar condensation to oxindoles.

H. W.

Preparation of Dihydroisoindole. JULIUS VON BRAUN and ANNEMARIE NELKEN (*Ber.*, 1922, **55**, [B], 2059—2063).—The preparation of dihydroisoindole, $\text{C}_6\text{H}_4\langle\text{CH}_2\rangle\text{NH}$, has hitherto been a matter of considerable difficulty. It has been shown, however, by Scholtz (A., 1898, i, 567) that dixylenium bromide, $\text{C}_6\text{H}_4\langle\text{CH}_2\rangle\text{NBr}\langle\text{CH}_2\rangle\text{C}_6\text{H}_4$, and *N*-xylylenepiperidinium bromide, $\text{C}_6\text{H}_4\langle\text{CH}_2\rangle\text{NBr}\langle\text{CH}_2\cdot\text{CH}_2\rangle\text{CH}_2$, are converted in a remarkable manner by ammonia into the compounds $\text{C}_6\text{H}_4\langle\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\rangle\text{C}_6\text{H}_4$ and $\text{C}_6\text{H}_4\langle\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\rangle\text{CH}_2$, respectively. Since many-membered rings containing nitrogen are not generally stable, it appeared probable that these compounds would be decomposed when further heated, with the formation of dihydroisoindole, on the one hand, and dihydroisoindole and piperidine on the other. This is found to be the case, and a convenient method of preparing dihydroisoindole is thus afforded; the intermediate isolation of the complex ring compounds is unnecessary.

N-Xylylenepiperidinium bromide is obtained in nearly 90% yield by the method of Scholtz; a greatly improved mode of obtaining dixylenium bromide is described. The conversion of the bromides into the cyclic imines has been examined in detail, as has also the action of heat on the latter. For the preparation of dihydroisoindole, however, it is preferable to heat xylylenepiperidinium bromide with one and a half times its quantity of ammonia (25%) during twenty-four hours at 200°; fractionation of the product gives piperidine, dihydroisoindole (yield 30%), and a complex residue. Di-*o*-xylylenecammonium bromide is heated with twice its quantity of ammonia (25%) for three to four hours at 250°; fractional distillation of the product gives dihydroisoindole, b. p. 90°/14 mm., in 25% yield, di-*o*-xylyleneimine in 22% yield, and a complex residue.

Di-*o*-xylyleneimine is conveniently identified as its *p*-nitrobenzoyl derivative, m. p. 167°; dihydroisoindole gives a characteristic benzoate, m. p. 100°.

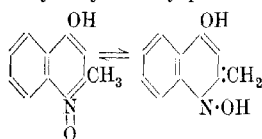
N-Phenyl dihydroisoindole, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{NPh}$, is readily prepared from *o*-xylylene bromide and aniline; it is converted by amyl nitrite in alcoholic solution in the presence of hydrochloric acid into the nitroso-compound, a green powder, m. p. 286–287°, from which dihydroisoindole could only be obtained in small yield by the action of sodium hydroxide or sodium hydrogen sulphite.

H. W.

Some New Derivatives of 2-Methylquinoline. K. LUCILLE MCCLUSKEY (*J. Amer. Chem. Soc.*, 1922, **44**, 1573–1577).—

4-Hydroxy-2-methylquinoline oxide, described recently by Gabriel and Gerhard (A., 1921, i, 441, 687), has been obtained independently by a rather different method; and several of its derivatives are described. The isolation of a dibenzoyl derivative of the compound necessitates a partial modification of the structure previously assigned to it, the most probable suggestion being that it is an equilibrium mixture (annexed formulæ).

Ethyl *o*-nitrobenzoylacetate is reduced by stannous chloride and hydrogen chloride in glacial acetic acid solution to ethyl 4-hydroxy-2-methylquinoline-3-carboxylate oxide, a colourless, crystalline substance, m. p. 174° [platinichloride, m. p. 203° (decomp.)]. It is hydrolysed by alkali hydroxide to 4-hydroxy-2-methylquinoline-3-carboxylic acid oxide, decomp. 209°, which passes by loss of carbon dioxide into 4-hydroxy-2-methylquinoline oxide, m. p. 247° (decomp.) after softening at 245° (platinichloride, m. p. 229–230° after darkening at about 200°; picrate, m. p. 171°; monobenzoyl derivative, m. p. 236°; dibenzoyl derivative, prepared by the action of benzoyl chloride and benzene on an alkaline solution of 4-hydroxy-2-methylquinoline oxide, a colourless, crystalline substance, m. p.



171°). 4-Hydroxy-2-methylquinoline oxide is reduced by zinc dust and hydrochloric acid to 4-hydroxy-2-methylquinoline.

o-Nitrobenzoylacetone is reduced in a similar manner to 4-hydroxy-2-methylquinoline oxide.

H. W.

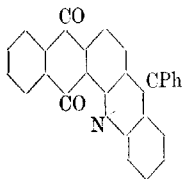
2:8-Tetramethyldiaminoacridine. KISHORI LAL MOUDGILL (T., 1922, 121, 1506—1509).

The Reaction of *o*-Halogenated Ketones with Feebly Basic Amines and Synthesis of Derivatives of *ms*-Phenylacridine. FRITZ MAYER and WALTER FREUND [with KASPAR PFAFF and HERMANN WERNECKE] (*Ber.*, 1922, 55, [B], 2049—2058).—The condensation of *o*-chlorobenzaldehyde with feebly basic amines has been described in a series of communications by Mayer and his co-workers (A., 1916, i, 843; 1918, i, 36; 1921, i, 175). The experiments have now been extended to *o*-halogenated ketones. Reaction occurs in accordance with the scheme: $R'CO-C_6H_4Cl + NH_2R \rightarrow R'CO-C_6H_4NHR + HCl$. *o*-Nitroamines of the benzene series, 2-nitro- α -naphthylamine, and anthraquinone derivatives which contain the amino-group in the α -position may be used. R' may be the methyl or phenyl group; in the latter case, ring closure may be effected with production of derivatives of *ms*-phenylacridine. Full directions are given for the preparation of *o*-chlorobenzophenone (cf. Overton, A., 1893, i, 208; Graebe and Keller, A., 1899, i, 703) and *o*-bromobenzophenone. 4-Chloro-3-acetyltoleuene (cf. Claus, A., 1891, 1222; 1892, 985) has b. p. 239—240°; it yields an oxime, m. p. 100—101° (Claus, m. p. 94°), and condensation products with *p*-chlorobenzaldehyde and anisaldehyde, m. p. 105—106° and 83—84°, respectively. The action of acetyl chloride on *p*-bromotoluene gives a ketone, b. p. 257—258° [oxime, m. p. 112—114° (Claus, m. p. 109°); semicarbazone, m. p. 224°; *p*-nitrophenylhydrazone, m. p. 173°], whereas *o*-bromotoluene yields a ketone, b. p. 262—264°/760 mm., 132—137°/12 mm. (oxime, m. p. 104°, semicarbazone, m. p. 224°, *p*-nitrophenylhydrazone, m. p. 203°); the semicarbazones of the two compounds are identical, whereas the oximes and *p*-nitrophenylhydrazones differ from one another. An unexplained abnormality in the course of the Friedel-Crafts' reaction is therefore indicated, but since the imino-ketones derived from the two ketones are identical, it follows, at any rate, that each contains 3-bromo-1-acetyltoleuene. Benzoylation of *p*-bromotoluene gives a ketone, b. p. 204°/12—13 mm. (oxime, m. p. 143—145°, and also a variety, m. p. 100°; semicarbazone, m. p. 168—172° after softening at 156°). *o*-Bromotoluene yields a ketone, b. p. 206°/15—16 mm. (oxime, m. p. 143—145°, and a variety, m. p. 79—80°, which is possibly not homogeneous; semicarbazone, m. p. 168—172° after softening at 164°). In this instance, the semicarbazones and oximes appear to be identical. It is possible that the ketones exist in stereoisomeric forms, but the greater probability appears to be that they are mixtures. Oxidation of either dibrominated ketone gives *p*-benzoylbenzoic acid.

The imino-ketones are generally prepared by heating a solution of the halogenated ketone and the requisite base in naphthalene

or nitrobenzene at 220° with dry sodium carbonate and a little copper powder. The acridines are obtained by heating the imino-ketones with concentrated sulphuric acid on the water-bath.

The following substances are derived from *o*-chlorobenzophenone: with *o*-nitroaniline, 1-nitro-5-phenylacridine, brownish-yellow leaflets, m. p. 218°; with 2:4-dinitroaniline, *o*-2':4'-dinitroanilinobenzoylbenzene, $C_6H_3(NO_2)_2 \cdot NH \cdot C_6H_4 \cdot C(=O)Ph$, yellow needles, m. p. 161—162°; 1:3-dinitro-5-phenylacridine, m. p. 240°; with 3-nitro-*p*-toluidine, *o*-2'-nitro-*p*-toluidinobenzoylbenzene, golden-yellow needles, m. p. 125—126°, and 1-nitro-5-phenyl-3-methylacridine, yellow needles, m. p. 202° (1-amino-5-phenyl-3-methylacridine, brown crystals); with 4-chloro-*o*-nitroaniline, *o*-2':4'-chloronitroanilinobenzoylbenzene, brownish-yellow needles, m. p. 124—125°, and 3-chloro-1-nitro-5-phenylacridine, golden-yellow needles, m. p. 251—252°; with 2-nitro- α -naphthylamine, *o*-2'-nitro- α -naphthylaminobenzoylbenzene, pale yellow needles, m. p. 273° (this is the only derivative of naphthalene which could be caused to react); with 1-aminoanthraquinone, *o*-anthraquinonyl-1'-aminobenzoylbenzene, brown crystals, m. p. 146° (also prepared from *o*-aminobenzophenone and 1-chloro-



anthraquinone) and anthraquinone-2:1-m-phenylacridine (annexed formula), yellowish-brown crystals, m. p. 273—274° (the sulphonic acid and a mononitro-derivative, reddish-brown crystals, m. p. 284—285°, are described); from 1-amino-2-methylantraquinone, *o*-2'-methylantraquinonyl-1'-aminobenzoylbenzene, dark red crystals, m. p. 173°; with 1:5-diaminoanthraquinone, bis-2'-benzoylanilino-1:5-anthraquinone, $C_{14}H_6O_2(NH \cdot C_6H_4 \cdot C(=O)Ph)_2$, dark red crystals, m. p. 248°, and anthraquinone-2:1:6:5-di-m-phenylacridine, bluish-black crystals; with 1-nitro-2-aminoanthraquinone, 1-nitroanthraquinone-3:2-m-phenylacridine, a pale brown powder.

o-Aminobenzophenone gives 5-phenylacridine, m. p. 179—180°, with iodobenzene; 5-phenyl-2:1-benzoacridine, yellow needles, m. p. (indefinite) 129°, with α -bromonaphthalene; and 5-phenyl-4:3-benzoacridine, m. p. 198°, with β -bromonaphthalene.

The following compounds are derived from 4-chloro-3-acetyl-toluene: with 2:4-dinitroaniline, *o*-2':4'-dinitroanilino-5-methylacetophenone, orange-coloured leaflets, m. p. 177—178°; with 1-aminoanthraquinone, *o*-anthraquinonyl-1'-amino-5-methylacetophenone, black needles, m. p. 209—210°; with 1-amino-4-hydroxyanthraquinone, *o*-4'-hydroxyanthraquinonyl-1'-amino-5-methylacetophenone, blackish-violet needles, m. p. 237—238°.

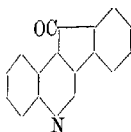
The action of 2:4-dinitroaniline on acetylated *o*- and *p*-bromotoluene gives *o*-2':4'-dinitroanilino-*p*-methylacetophenone, brownish-yellow, lustrous leaflets (m. p. 236° and 240°, respectively, mixed m. p. 237°).

Benzoylated *o*- and *p*-bromotoluenes are transformed by 2:4-dinitroaniline into *o*-2':4'-dinitroanilino-*p*-methylbenzophenone, orange-coloured needles or leaflets (m. p. 143° and 141—142°, respectively,

m. p. of mixture, 142–143°), from which 7:9-dinitro-5-phenyl-3-methylacridine, pale yellow crystals, m. p. 273°, is derived. With 3-nitro-*p*-toluidine they give *o*-2':4'-nitro-4'-methylanilino-*p*-methylbenzophenone, reddish-yellow crystals, m. p. 133.5°, which is converted into 9-nitro-5-phenyl-2:7-dimethylacridine, a pale yellow, microcrystalline powder, decomp. 241°.

2-Chloro-5-methylbenzophenone is transformed by 2:4-dinitroaniline into *o*-2':4'-dinitroanilino-5-methylbenzophenone, yellow needles, m. p. 136–137°. 7:9-Dinitro-5-phenyl-3-methylacridine crystallises in needles, m. p. 285–287°; the corresponding diamino-compound forms reddish-brown needles, m. p. 151°. H. W.

Preparation of Ring Ketones of the Quinoline Series. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 343322; from *Chem. Zentr.*, 1922, ii, 146–147).—Ring ketones of the quinoline series are prepared by the action of sulphuric acid on derivatives of 3-phenylquinoline-4-carboxylic acid, which thereby pass into ring ketones of the general formula



(annexed). 2-Hydroxy-3-phenylquinoline-4-carboxylic acid when heated with concentrated sulphuric acid for two hours at 100° yields a ring ketone in the form of orange-red crystals, m. p. much above 300°: it may be sublimed at higher temperatures. 2-Hydroxy-3-phenylquinoline-4-carboxylic acid is obtained by condensation, in the presence of alkali, of isatin with phenylacetyl chloride or anhydride, phenylacetyl- ψ -isatin being formed as an intermediate product. It forms light yellow needles which decompose on melting. 2:3-Diphenylquinoline-4-carboxylic acid gives similarly a yellow ring ketone. G. W. R.

Preparation of Diaminodinaphthyl- and Dinaphthacarbazole-sulphonic Acids. KALLE & Co., AKT.-GES. (D.R.-P. 343149; from *Chem. Zentr.*, 1922, ii, 144).—1:1'-Azonaphthalenesulphonic acids are treated with acid or alkaline reducing agents. For example, 1:1'-azonaphthalene-5:5'-disulphonic acid by reduction with tin and hydrochloric acid gives 1:1'-diamino-2':2'-dinaphthyl-5:5'-disulphonic acid. It forms colourless needles and gives a yellow diazo-compound with nitrous acid. By the action of sodium amalgam in weak alkaline solution, 1:1'-diamino-2:2'-dinaphthyl is formed, which by heating with hydrochloric acid readily gives dinaphthamine [*di- $\alpha\beta$ -naphthacarbazole*]. On heating the acid with hydrochloric acid at 140°, ammonia is eliminated. 1:1'-Azonaphthalene-4:4'-disulphonic acid gives, by reduction with a hot alkaline sodium thiosulphate, an acid crystallising in fine needles which cannot be diazotised, and on heating with mineral acids at 130° gives *di- $\alpha\beta$ -naphthacarbazole*. It is therefore supposed to be *di- $\alpha\beta$ -naphthacarbazole-5:8-disulphonic acid*. The reduction product from 2:2'-azonaphthalene-7:7'-disulphonic acid crystallises in compact, colourless needles and gives with nitrous acid a yellow tetra-azo-compound. On heating with mineral acids at 130°, the 2:2'-diamino-1:1'-dinaphthyl-7:7'-disulphonic acid gives *di- $\beta\gamma$ -naphthacarbazole* with intermediate

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formation of di- α -naphthacarbazole-2:12-disulphonic acid. The products are used in the preparation of colouring matters.

G. W. R.

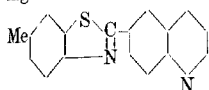
A New Mode of Formation of Thiazole Derivatives of the Anthraquinone Series. EDUARD KOPETSCHNI and HERTA WIESLER (*Monatsh.*, 1922, **43**, 81—87).—When heated with aqueous or alcoholic ammonia, 2-amino-1-thiolanthraquinone is converted into 2-aminoanthraquino-1-thiazole (cf. Gattermann, A., 1912, i, 1004), which forms microscopic needles, m. p. 285° (not sharp), and gives an *acetyl* derivative, which forms olive-yellow needles, m. p. 294°. Oxygen must enter at some stage in the formation of the thiazole, and it is probable that the first step consists in the oxidation of the mercaptan to 2:2'-diaminodianthraquinone 1:1'-disulphide, since this substance also is converted into the thiazole on treatment with ammonia. Dianthraquinonyl 1:1'-disulphide behaves similarly, giving the thiazole previously obtained by Gattermann (*loc. cit.*). 3:3'-Dichloro-2:2'-diaminoanthraquinone 1:1'-disulphide yields 3-chloro-2-aminoanthraquino-1-thiazole, blue needles, m. p. 322—324° (decomp.), which, in contrast with 2-aminoanthraquino-1-thiazole, is sulphonated with difficulty.

C. K. I.

Thiazoles. II. 1-*p*-Tolybenzothiazole, Dehydrothio-*p*-toluidine and some Related Compounds. MARSTON TAYLOR BOGERT and MARTIN MEYER (*J. Amer. Chem. Soc.*, 1922, **44**, 1568—1572).—1-*p*-Tolybenzothiazole, $C_6H_4 < \begin{smallmatrix} S \\ N \end{smallmatrix} > C-C_6H_4Me$, colourless needles, m. p. 85° (corr.), is prepared in 60—75% yield by the oxidation of thio-*p*-toluanilide, m. p. 142° (corr.), by aqueous potassium ferricyanide; it cannot be obtained satisfactorily by fusing *p*-toluanilide with sulphur in the presence or absence of naphthalene. It is practically odourless when dry (in striking contrast to the corresponding phenyl derivative), but has a faint odour of roses when moistened with alcohol. It is converted by nitric and sulphuric acids into the *mononitro*-derivative, $NO_2C_{14}H_{10}NS$, pale, cream-coloured needles, m. p. 219.5° (corr.), which is reduced by zinc or tin and hydrochloric acid to the *amino*-compound, $NH_2C_{14}H_{10}NS$, pale brown crystals, m. p. 229° (corr.). The diazotised amine couples on the fibre with a considerable variety of the commoner azo-couplers, and thus yields mono- and bis-azo-dyes which compare very favourably with the corresponding dyes from the isomeric dehydrothio-*p*-toluidine in fastness to light, to soaping, to bleaching, etc., and are in some case superior in tinctorial power. 1-*p*-Tolybenzothiazole is oxidised by potassium permanganate in neutral or alkaline solution to (?) *benzothiazoyl*-1-*p*-benzoic acid, microscopic, colourless needles, which darken but do not melt at 270°.

Diazotised primuline couples on the fibre with benzoylenecarbamide, giving a *product* which dyes unmordanted cotton a direct yellowish-brown of good fastness to acids, alkalis, or bleach, but quite fugitive to daylight.

Dehydrothio-*p*-toluidine [1-*p*-aminophenyl-5-methylbenzothiazole] is readily converted into the corresponding *benzylidene* derivative, $\text{C}_6\text{H}_5\text{Me} \langle \text{S} \rangle \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{CHPh}$, almost colourless, glistening leaflets, m. p. 193° (corr.).



p-Nitrobenzylidene-*p*-toluidine, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, pale yellow needles, m. p. 123° (corr.), could not be converted into dehydrothio-*p*-toluidine by fusion with sulphur. The conversion of dehydrothio-*p*-toluidine into the corresponding atophan could not be effected.

6-(5-Methylbenzothiazolyl)quinoline, microscopic, pale brown crystals, m. p. 147° (corr.), is prepared by the action of concentrated sulphuric acid, glycerol, and arsenic acid on dehydrothio-*p*-toluidine. (See also *Chem. News*, 1922, 124, 319–323, 328–330, 344–346, 360–361, 376–381, 391–395; 125, 2–5, 19–22.) H. W.

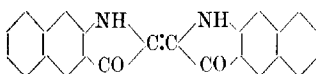
The Iron Salts of Dipyrrolylphenylmethane Dyes and Triphenylpyrrolylmethane. II. Diphenylpyrrolylcarbinol and its Derivatives. HANS FISCHER and MARIA KAAH (*Z. physiol. Chem.*, 1922, 120, 267–276; cf. this vol., i, 276).—Ethyl 2:4-dimethylpyrrole-3:5-dicarboxylate reacts with magnesium phenyl bromide in ethereal solution to form 3-carbethoxy-2:4-dimethylpyrrolyldiphenylcarbinol, $\text{OH} \cdot \text{CPh}_2(\text{C}_2\text{NHMe}_2 \cdot \text{CO}_2\text{Et})$, pure white, long, blunt needles, m. p. 156° , easily soluble in the usual organic solvents. It forms an orange *picrate*, $\text{C}_{22}\text{H}_{21}\text{O}_9\text{N}_3\text{C}_6\text{H}_5\text{O}_3\text{N}_3$, m. p. 181° (decomp.), which is apparently really the picrate of the dye, $\text{C}_{22}\text{H}_{21}\text{O}_9\text{N}_3$, fine, yellow needles, m. p. 178° , formed from the carbinol on boiling with acetic acid. This compound, however, which presumably has the formula $\text{CPh}_2 \cdot \text{C}(\text{CMe})_2 \cdot \text{N} : \text{CMe} > \text{C} \cdot \text{CO}_2\text{Et}$, forms no picrate directly.

The carbinol can be reduced catalytically with hydrogen and platinum to form 3-carbethoxy-2:4-dimethylpyrrolyldiphenylmethane, m. p. 138° . The constitution of this compound is proved by the fact that it is obtained from diphenylcarbinol and ethyl 2:4-dimethylpyrrole-3-carboxylate on boiling in acetic acid. Ethyl 2:3:5-trimethylpyrrole-4-carboxylate does not react with magnesium phenyl bromide.

p-Anisyl-bis(3-carbethoxy-2:4-dimethylpyrrolyl)methane, formed from the condensation of anisaldehyde and ethyl 2:4-dimethylpyrrole-3-carboxylate, melts at 170° [cf. Feist, A., 1902, i, 491]. From terephthalaldehyde and ethyl 2:5-dimethyl-3-pyrrolylcarboxylate, *p*-bis(3-carbethoxy-2:5-dimethylpyrrolyl)methylbenzaldehyde is obtained, m. p. 202.5° (hydrazone, $\text{C}_{32}\text{H}_{36}\text{O}_4\text{N}_4$). W. O. K.

2:2'-ββ-Naphthindigotin. HANS EDUARD FIERZ and RICHARD TOBLER (*Helv. Chim. Acta*, 1922, 5, 557–560).—2:2'-ββ-Naphthindigotin was prepared by the usual series of reactions for comparison with other dyes of the naphthindigotin series. It was found that 3-hydroxy-β-naphthoic acid could be converted into 3-amino-β-naphthoic acid in good yield by heating with ammonium chloride and zinc chloride ammoniate in a current of ammonia at

180—190°. The presence of zinc oxychloride induces side reactions with formation of β -naphthylamine and dinaphthacridone. The aminonaphthoic acid is converted quantitatively into the corresponding glycine by condensing with chloroacetic acid. β -Naphthylglycine-3-carboxylic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$, crystallises from alcohol in groups of yellow needles, m. p. 240°. The hygroscopic sodium salt crystallises from concentrated solution in yellowish-



brown needles. Very poor yields of the naphthindigotin are obtained from the glycine by any of the usual methods;

2:2'- β -naphthindigotin (annexed formula) crystallises from nitrobenzene in nearly black tablets. When brominated, it takes up three atoms of bromine, but the resulting dye is not fast to chlorine [cf. *J. Soc. Chem. Ind.*, 1922, **41**, 625A.].

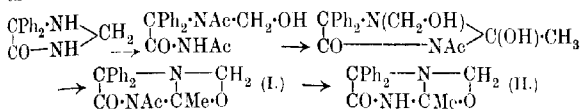
E. H. R.

Attempts to Prepare *peri*-Naphthindigotin, and the Behaviour of Azo-dyes from Naphthylglycines.

HANS EDUARD FIERZ and RICHARD SALLMANN (*Helv. Chim. Acta*, 1922, **5**, 560—566).—Attempts to prepare a *peri*-naphthindigotin from α -naphthylglycine-8-carboxylic acid were unsuccessful, owing to the instability of the naphthylglycines, which is reflected in the ease with which azo-dyes prepared from them are decomposed. In the preparation of naphthastyril from naphthalimide by oxidation with sodium hypochlorite, the maximum yield obtained was 50%. By condensation of naphthastyril with chloroacetic acid, naphthastyrilacetic acid, m. p. 256°, was obtained, which by boiling with sodium ethoxide was converted into disodium α -naphthylglycine-8-carboxylate, a white powder. α -Naphthylglycine-8-sulphonic acid was prepared by condensing α -naphthylamine-8-sulphonic acid with chloroacetic acid, and forms colourless needles containing $1\text{H}_2\text{O}$. α -Naphthylglycine-4-sulphonic acid has a yellow colour, and crystallises with $1\text{H}_2\text{O}$; in alkaline solution, it shows a strong blue fluorescence. α -Naphthylglycine-5-sulphonic acid crystallises in anhydrous, colourless leaflets or needles, and shows a green fluorescence in alkaline solution. β -Naphthylglycine-1-sulphonic acid crystallises with $2\text{H}_2\text{O}$ in colourless, fan-shaped aggregates of needles. The azo-dyes from all these naphthylglycinesulphonic acids are decomposed by boiling water. The α -4-acid does not couple readily with diazo-compounds; with diazobenzene in alkaline solution it forms a crystalline additive compound. The decomposition of azo-dyes derived from β -naphthylglycine ethyl ester was studied particularly. Benzeneazo- β -naphthylglycine ethyl ester, $\text{C}_{20}\text{H}_{19}\text{O}_2\text{N}_3$, forms bright red needles, m. p. 135°. *p*-Nitrobenzeneazo- β -naphthylglycine ethyl ester, $\text{C}_{20}\text{H}_{18}\text{O}_4\text{N}_4$, forms brown or bronze needles, decomposing at 156°; in glacial acetic acid it gives a violet colour and in sulphuric acid cherry-red. From the decomposition products of the latter when boiled with acetic acid were isolated the following: ethyl 2-*p*-nitrophenyldihydro-1:2:4-isonaphthatriazine-3-carboxylate, $\text{C}_6\text{H}_4\text{—}\overset{\text{C}_6\text{H}_4\text{—N}}{\underset{\text{CH:CH—C—N—CH—CO}_2\text{Et}}{\text{N}}}$, m. p. 210°, naphthiminazole, and *p*-nitroaniline.

E. H. R.

Decompositions Occurring in the Acylation of 5:5-Diphenyltetrahydro-4-glyoxalone. HEINRICH BILTZ, KARL SEYDEL, and EDITH HAMBURGER-GLAZER (*Annalen*, 1922, **428**, 198—243).—Following previous work, the authors describe a detailed study of the acetylation and formylation products of 5:5-diphenyltetrahydro-4-glyoxalone (A., 1912, i, 909), and conclude that dieyclic substances are thus produced. For instance, the reaction with acetyl chloride takes the following course:



The product (I) on hydrolysis loses an acetyl group, giving (II), with which the decompositions described below were carried out.

5:5-Diphenyl-1:2-dimethyltetrahydro-4-glyoxalone-1':2-oxide (II), tablets, m. p. 204—205°, on acetylation, gives the 3-acetyl derivative (I), m. p. 203—204°, from which it was originally obtained, and on benzoylation, yields a 3-benzoyl derivative, needles, m. p. 172°, which on hydrolysis gives back the original oxide. On condensation with phenylcarbimide, the oxide gives a substance, $\text{C}_{24}\text{H}_{21}\text{O}_3\text{N}_3$, m. p. 210°, and on methylation with methyl sulphate it yields a 3-methyl derivative, m. p. 177°, from which the methyl group is not removed by Zeisel's method. That the replaceable imino-hydrogen atom which takes part in these reactions is in position 3 is proved by the oxidation of the methyl derivative to 5:5-diphenyl-3-methylhydantoin by means of chromic oxide and acetic acid, and by its hydrolytic fission, on fusion with potassium hydroxide, to diphenylmethyamine, methylamine, and carbon dioxide. The oxide (II) itself gives 5:5-diphenylhydantoin on oxidation by permanganate, and on reduction by means of hydriodic acid yields diphenylacetamide and an isomeric (or polymeric) substance, m. p. 252°, the constitution of which is not clear.

Recognition of the 2-methyl group was effected through a study of 4:4-diphenyl-2-methyl-4:5-dihydro-5-glyoxalone, m. p. 228—229°, which is obtained from the oxide (II), along with diphenylhydantoin, by cautious oxidation by alkaline permanganate. This substance is amphoteric (*hydrochloride*, m. p. 280°, decomp.) and on further oxidation with chromic oxide and acetic acid gives diphenylhydantoin; it yields a 1-acetyl derivative, monoclinic crystals, m. p. 149—150°, which on hydrolysis loses its acetyl group, reforming the original dihydroglyoxalone, and a 1-methyl derivative, m. p. 171—172° (sinters at 169°), which on oxidation by chromic oxide and acetic acid yields 5:5-diphenyl-3-methylhydantoin. On reduction by sodium amalgam or sodium and alcohol, the dihydroglyoxalone is converted into 5:5-diphenyl-2-methyltetrahydro-4-glyoxalone, prisms, m. p. 180—181° (*perchlorate*, leaflets, m. p. 235°, decomp.), which, on oxidation by permanganate again yields the dihydroglyoxalone, and on acetylation yields a 1:3-diacetyl derivative, m. p. 193°, hydrolysable to the original tetrahydro-

glyoxalone. The formation of this compound is clear proof that the methyl group must be in the 2-position, whence the orientation of the original dihydroglyoxalone and of its parent oxide follows. On oxidation by alkaline permanganate at the ordinary temperature the above dihydroglyoxalone is converted into 4:4-diphenyl-4:5-dihydro-5-glyoxalone-2-carboxylic acid, which on heating begins to decompose at about 65–66°, giving 4:4-diphenyl-4:5-dihydro-5-glyoxalone (*loc. cit.*).

In the previous paper it was noted that a by-product, $C_{19}H_{18}O_4N_2$, m. p. 224–225°, was obtained when the diphenyl-dihydroglyoxalone was acetylated (*Annalen*, 1912, **391**, 225). It is now evident that this substance is 3-formyl-1-acetyl-2-hydroxy-5:5-diphenyl-2-methyltetrahydro-4-glyoxalone, and that it is formed as a result of a preliminary ring-fission as with the oxides described in this paper. Confirmation is found in the fact that the substance yields 4:4-diphenyl-2-methyl-4:5-dihydro-5-glyoxalone on hydrolysis.

The action of formic acid on 5:5-diphenyltetrahydro-4-glyoxalone gives rise to 5:5-diphenyl-1-methyltetrahydro-4-glyoxalone 1':2-oxide, which forms glistening, hexagonal leaflets, m. p. 260°. The substance is hydrolysed by hydrobromic or hydriodic acid to the original tetrahydroglyoxalone, and is oxidised by alkaline permanganate to 5:5-diphenylhydantoin. Its 3-acetyl derivative, m. p. 127°, and 3-benzoyl derivative, m. p. 176°, are each hydrolysable to the original oxide, whilst the 3-methyl derivative, m. p. 146°, obtained with the aid of methyl sulphate, is oxidised by permanganate or chromic acid to 5:5-diphenyl-3-methylhydantoin, and is hydrolysed by hydrobromic acid to 5:5-diphenyl-3-methyltetrahydro-4-glyoxalone, which forms hexagonal prisms, m. p. 90°.

The action of formic acid on 5:5-diphenyl-2-methyltetrahydro-4-glyoxalone gives rise to 5:5-diphenyl-1-ethyltetrahydro-4-glyoxalone 1':2-oxide, small needles, m. p. 256°, which on oxidation by chromic oxide in acetic acid gives 5:5-diphenylhydantoin, and, on hydrolysis by means of hydrobromic acid, yields 5:5-diphenyl-2-methyltetrahydro-4-glyoxalone.

4:4-Diphenyl-1-methyl-4:5-dihydro-5-glyoxalone on oxidation with chromic acid gives 5:5-diphenyl-3-methylhydantoin, and on reduction yields 5:5-diphenyl-3-methyltetrahydro-4-glyoxalone, which, on oxidation, gives the same hydantoin. In view of these facts and others recorded above, the constitutions previously assigned (*loc. cit.*) to 4:4-diphenyl-4:5-dihydro-5-glyoxalone must be revised in the sense indicated by the name now employed. The substance was previously regarded as 5:5-diphenyl-4:5-dihydro-4-glyoxalone by reason of its fission by alkalis to "methylamino-diphenylacetic acid," but it is now held that the constitution of this substance is uncertain, since attempts to synthesise it have not yet been successful.

C. K. I.

Preparation of isoPropylallylbarbituric Acid. F. HOFFMANN-LA ROCHE & Co. (Brit. Pat. 181247).—isoPropylallylbarbituric acid is obtained in 80% yield by the action of allyl bromide

(130 parts) on a solution of isopropylbarbituric acid (170 parts) in 500 parts of water and 135 parts of 30% sodium hydroxide at 25° for twelve hours. The product is collected and crystallised from dilute alcohol. It is sparingly soluble in water, readily soluble in alcohol and ether, and melts at 137—138°. G. F. M.

The Methylalkylpyridazinonecarboxylic Esters. H. GAULT and T. SALOMON (*Compt. rend.*, 1922, **175**, 274—277).—*Ethyl 3-methyl-6-pyridazinone-5-carboxylate* is obtained by the reaction in the cold of equimolecular proportions of hydrazine hydrate and ethyl acetonilmalonate in absolute alcoholic solution. It is a crystalline substance soluble in water, m. p. 76—77°. The hydrazide of the corresponding acid is obtained if 2 mols. of hydrazine are used in the above reaction. It is a white substance, m. p. 153°. The above ester readily gives a sodium derivative which condenses with alkyl iodides to give 3-methyl-5-alkylpyridazinonecarboxylic esters. *Ethyl 3-methyl-5-ethylpyridazinone-5-carboxylate* prepared in this way melts at 72°. On hydrolysis with 10% sodium hydroxide in the cold, it gives the corresponding acid, m. p. 130°, which on heating loses carbon dioxide, giving the methylalkylpyridazinone. *3-Methyl-6-pyridazinone* melts at 94°, and both it and its alkyl derivatives on treatment with dilute mineral acid are converted into α -alkyl-lævulic acids. G. F. M.

Spirans. X. Proof of the Peculiar Spiran Asymmetry by the Preparation of an Optically Active Spiran. HERMANN LEUCHS, EVA CONRAD, and HANS VON KATINSZKY (*Ber.*, 1922, **55**, [B], 2131—2139).—Although bishydrocarbostyryl-3:3'-spiran, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \cdot \text{CO} \end{smallmatrix} > C \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \cdot \text{NH} \end{smallmatrix} < C_6H_4$ (this vol., i, 471), does not contain an asymmetric carbon atom, it does not possess a plane of symmetry, since the planes of the two rings are at right angles to one another and it should therefore exist in two enantiomorphous, optically active forms. The spiran itself is neutral in character and scarcely suitable for experimental resolution. The communication is devoted to a description of compounds prepared for the purpose of introducing basic or acidic substituents into the molecule and of the resolution of a disulphonic acid into its optically active forms.

Di-p-bromodihydrocarbostyryl-3:3'-spiran, colourless, hexagonal leaflets which do not melt below 300°, is prepared by the action of bromine on the parent spiran in boiling glacial acetic acid solution. *Di-op-dichlorodihydrocarbostyryl-3:3'-spiran* crystallises in colourless, hexagonal leaflets which are unchanged at 290°. *Di-p-nitrodihydrocarbostyryl-3:3'-spiran*, from the spiran and concentrated nitric acid at 70°, forms yellow leaflets which do not melt below 290°, whereas *di-op-dinitrodihydrocarbostyryl-3:3'-spiran*, from the spiran and nitric and sulphuric acids at 0°, crystallises in pale yellow needles which darken without melting above 280°. *Bis-dihydrocarbostyryl-3:3'-spiran-6:6'-disulphonic acid*, colourless, quadratic plates (+aq), m. p. 105—115° after softening at 80°.

$h \ h^*$

re-solidification at 140–150°, and decomp. about 260° after becoming yellow at 220°, is prepared by the action of cold concentrated sulphuric acid on the spiran; the corresponding *barium* salt, $C_{17}H_{12}O_8N_2S_2Ba \cdot 8H_2O$, is described. The acid is resolved by quinine in methyl alcoholic solution; from the product the quinine salt of the *l*-acid separates first. *l-Bisdihydrocarbostyryl-3:3'*. *spiran-6:6'-disulphonic acid* crystallises in needles (+6H₂O), m. p. 230–235° (decomp.) after softening at 200°; $[\alpha]_D^{25} -233.8^\circ$ in aqueous solution; the corresponding *barium* salt (+6H₂O) has $[\alpha]_D^{25} -189.6^\circ$ in water. *Barium d-bisdihydrocarbostyryl-3:3'*. *spiran-6:6'-disulphonate* has $[\alpha]_D^{25} +192.2^\circ (\pm 2.6^\circ)$ in aqueous solution.
H. W.

Brominated isoCyanines. KISHORI LAL MOUDGILL (T., 1922, 121, 1509–1511).

The Action of Hydroxylamine and of Hydrazine on the Aryl Monothioamides of Ethyl Acetylmalonate. DAVID E. WORRALL (*J. Amer. Chem. Soc.*, 1922, 44, 1551–1557).—The additive compounds of ethyl acetylmalonate and phenyl-, *p*-bromophenyl-, and *p*-tolyl-thiocarbimides react with hydroxylamine and hydrazine to form, respectively, *isooxazoles* and *pyrazoles*.

3-*Anilino-5-ketisooxazole*, $O \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{N} = \text{C} \cdot \text{NPh} \end{smallmatrix}$, slender, cream-coloured needles, m. p. 186° (decomp.) when rapidly heated (it darkens above 165° and is changed completely to a black tar at 180° when heated), is prepared by the action of two equivalent proportions of hydroxylamine on ethyl acetylmalonatemonothioanilide in boiling alcoholic solution. It forms a *sodium* salt and a *hydrochloride*, m. p. 135° (gas evolution). It is converted by nitrous acid into 3-*anilino-4-oximino-5-ketisooxazole*, slender, scarlet needles which deflagrate at 149°. With benzenediazonium chloride, it yields 4-*benzeneazo-3-anilino-5-ketisooxazole*, yellow needles, m. p. 195–197° (decomp.). Benzaldehyde converts it into 4-*benzylidene-3-anilino-5-ketisooxazole*, orange-coloured needles, m. p. 170–171°. The *isooxazole* is converted by acetic anhydride into the 2(or 5)-*acetyl* derivative, colourless plates or flattened needles, m. p. 145–146°, and by benzoyl chloride and sodium hydroxide into the *benzoyl* compound, colourless, lustrous needles, m. p. 157–158°.

Ethyl acetylmalonatemonothioanilide is transformed by two equivalent proportions of hydrazine into 3-*anilino-5-ketopyrazole*, $NH \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{N} = \text{C} \cdot \text{NPh} \end{smallmatrix}$, minute, colourless plates, decomp. 255–256°. Its *sodium* salt, *hydrochloride*, *benzoyl* derivative, and *acetyl* compound, needles, m. p. 101°, are described. The *oximino*-derivative crystallises in brilliant, red needles. With benzenediazonium chloride, it gives an *azo-compound*, maroon-coloured, irregular plates, decomp. 211–212°.

3-*p-Toluidino-5-ketisooxazole* forms diamond-shaped, pale yellow

crystals which blacken and foam at 155–156° after darkening above 145°; the sodium salt, hydrochloride, oximino-derivative, orange-coloured needles, decomp. 142°, and acetyl compound, colourless, slender needles, m. p. 149–150°, are described.

3-p-Toluidino-5-ketopyrazole crystallises in small, glistening, square plates, decomp. 246–247°; the hydrochloride, lustrous plates, m. p. 72–73°, and acetyl compound, m. p. 178–179° after softening, are described.

3-p-Bromoanilino-5-ketoisoxazole forms slender, cream-coloured needles, decomp. 188–189° after softening at 150°. 3-p-Bromoanilino-5-ketopyrazole crystallises in minute, colourless plates, m. p. 234–235° (decomp.).

Thioacetoacetyl-o-toluidide, $\text{COMe}\cdot\text{CH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, is converted by hydroxylamine mainly into thioacetyl-o-toluidide, hydroxyl amine acetate being also formed.

Ethyl acetylmalonate monothioanilide and phenylhydrazine give mainly acetylphenylhydrazide, m. p. 128°. H. W.

Constitution of the so-called Dithiourazole of Martin

Freund. I. PRAPHULLA CHANDRA GUHA (*J. Amer. Chem. Soc.*, 1922, 44, 1502–1510).—Dithiourazole, $\text{C}_2\text{H}_3\text{N}_3\text{S}_2$, has been prepared by Freund and his co-workers (A., 1894, i, 97; 1895, i, 400; 1896, i, 415) by the action of hydrochloric acid on hydrazodithio-

dicarbonamide, and the constitution $\text{NH} \begin{smallmatrix} \text{CS}\cdot\text{NH} \\ \text{CS}\cdot\text{NH} \end{smallmatrix}$ has been assigned to it without experimental evidence being adduced. It is now shown, however, that Freund's dithiourazole contains only one atom of hydrogen replaceable by metals such as potassium, sodium, or silver, and that it loses only one atom of hydrogen from each molecule when treated with ferric chloride, hydrogen peroxide, or iodine with formation of a disulphide, $(\text{C}_2\text{H}_2\text{N}_3\text{S})_2\text{S}_2$, the molecular complexity of which is established by determination of the molecular weight of the allyl derivative. These observ-

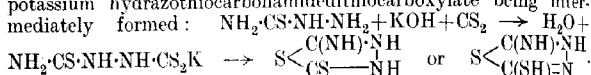
ations are in harmony with the formula $\text{S} \begin{smallmatrix} \text{C}(\text{SH})=\text{N} \\ \text{C}(\text{NH})\cdot\text{N} \end{smallmatrix}$ or $\text{S} \begin{smallmatrix} \text{C}(\text{SH})=\text{N} \\ \text{C}(\text{NH}_2)\cdot\text{N} \end{smallmatrix}$, for dithiourazole. The existence of a diacetyl compound from which one acetyl radicle is removed with great readiness, whereas the other is firmly retained, is thereby explained as well as the conversion of the monoacetyl derivative into a diacetyl disulphide and into monoacetylalkyl compounds. The reason of the failure of previous workers to obtain dialkyldithiourazoles analogous to the diacetyl derivatives is now rendered obvious.

5-Amino-2-thiol-1:3:4-thiodiazole is prepared conveniently by Freund's method, but the yields are greatly improved if the action of the acid is interrupted after ten minutes instead of after an hour. The following derivatives do not appear to have been described previously: the sodium and silver salts; the compound, $\text{C}_2\text{H}_2\text{N}_3\text{S}\cdot\text{SHg}(\text{NO}_2)_2$, from the parent substance and mercuric

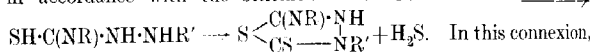
nitrite (cf. Rây and Guha, T., 1919, **115**, 261, 541), and the derivative, $C_6H_{12}N_3S_3Hg$, from the nitromercaptide and ethyl iodide (cf. Rây, T., 1916, **109**, 698).

5-Amino-2-thiol-1:3:4-thiodiazole is decomposed by concentrated hydrochloric acid at 190—200° into hydrazine dihydrochloride, ammonium chloride, carbon disulphide, and carbon dioxide. H. W.

Constitution of the so-called Dithiourazole of Martin Freund. II. New Methods of Synthesis, Isomerism, and Poly-derivatives. PRAPHULLA CHANDRA GUHA (*J. Amer. Chem. Soc.*, 1922, **44**, 1510—1517; cf. preceding abstract).—The only method available hitherto for the preparation of the so-called dithiourazoles consists in the elimination of ammonia from hydrazo-dithiocarbonamides by the action of concentrated hydrochloric acid, when, simultaneously, iminodithiourazole is formed by loss of hydrogen sulphide. It is now shown that dithiourazole (amino-thiodiazoethiol) is produced readily from thiosemicarbazide, carbon disulphide, and alcoholic potassium hydroxide solution, potassium hydrazothiocarbonamidethiocarboxylate being inter-



The method has been found to apply to all substituted and unsubstituted thiosemicarbazides when used in a slightly modified form. Except in the case of thiosemicarbazide itself, the potassium salt of the dithiocarboxylic acid is rarely formed, but, on continued heating, all the thiosemicarbazides without exception yield the corresponding thiodiazole derivatives. Reaction probably occurs in accordance with the scheme: $\text{R}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{NHR}' \xrightarrow{\text{CS}_2 + \text{alkali}}$



In this connexion, the synthesis of aminothiodiazoethiol from thiosemicarbazide by the direct action of carbon disulphide is of special significance, since 2:5-dithiotetrahydro-1:3:4-thiodiazole is also formed in small quantity by the action of the liberated hydrogen sulphide on the thiodiazole compound at a high temperature. The second method of synthesis is not of general application. It appears essential that the 1-position of the thiosemicarbazide should always be unsubstituted or substituted by positive groups such as methyl or ethyl; in other words, the basic character of the thiosemicarbazide should be kept unimpaired, so that carbon disulphide can combine with it directly.

The following substances have been prepared. 5-Imino-2-thio-4-phenyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, dull yellow needles, m. p. 183° (from 1-phenylthiosemicarbazide, carbon disulphide, and potassium hydroxide in absolute methyl alcoholic solution). 5-Phenylimino-2-thio-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 208°. 6-Phenylimino-2-thio-3-phenyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 202°. 5-Tolylimino-2-thio-

3-tolyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 205°. 5-Naphthylimino-2-thio-3-naphthyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 218°. 5-Tolylimino-2-thio-3-phenyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 188—189°. 5-Phenylimino-2-thio-3-tolyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 222°. 5-Naphthylimino-2-thio-3-phenyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 219°. 5-Phenylimino-2-thio-3-naphthyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 261°. 5-Naphthylimino-2-thio-3-tolyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 217°. 5-Tolylimino-2-thio-3-naphthyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 268°. 5-Allylimino-2-thio-3-phenyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 145°. 5-Allylimino-2-thio-3-tolyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, dull yellow needles, m. p. 125—126°. 5-Methylimino-2-thio-4-phenyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, dull yellow crystals, m. p. 142—143°. 5-Methylimino-2-thio-4-tolyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, dull yellow needles, m. p. 174—175°. 5-Methylimino-2-thio-3-naphthyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 183°. 5-Methylimino-2-thio-4-naphthyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 175°.

Potassium thiosemicarbazidedithiocarbonylate is prepared by heating at 70—75° an alcoholic solution of equivalent amounts of thiosemicarbazide, carbon disulphide, and potassium hydroxide; it is converted by iodine into aminothiodiazoethiol disulphide.

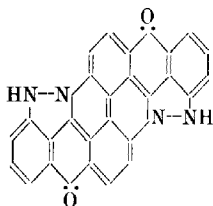
Thiosemicarbazide and carbon disulphide at 150° form aminothiodiazoethiol and dithiotetrahydrothiodiazole, m. p. 167°.

Freund's dithiourazole, m. p. 245°, had m. p. 232° after being preserved during about two months; either variety, when heated with hydrochloric acid at 150°, gave a *modification*, brownish-yellow, rectangular crystals, m. p. 224°.

Freund and Ingart obtained "phenyldithiourazole" in the form of colourless leaflets, m. p. 219°; de-acetylation of acetylphenyliminothiothiodiazole gives a tautomeric *variety*, dull yellow needles, m. p. 207°.

Acetylphenyliminothiotetrahydrothiodiazole has m. p. 244° (Freund and Ingart give 252°) when freshly prepared; after being preserved during several weeks it has m. p. 236°. The latter *variety* is also formed when the corresponding diacetyl compound is heated at 175° during five minutes. H. W.

The Constitution of Pyrazoleanthrone-yellow. FRITZ MAYER and RUDOLF HEIL (*Ber.*, 1922, 55, [B], 2155—2164).—Pyrazoleanthrone-yellow (cf. A., 1913, i, 533) is prepared by the mild action of potassium hydroxide on pyrazoleanthrone and was initially regarded as a derivative of indanthrene. Analyses of the dye, however, agree with the formula $C_{28}H_{12}O_2N_4$ or $C_{28}H_{14}O_2N_4$, according to which two molecules of pyrazoleanthrone are united with loss of two or four atoms of hydrogen. The formation of a potassium salt, of mono- or di-benzyl or substituted benzyl derivatives, and of a dibenzoyl compound proves that the replaceable hydrogen atoms of pyrazoleanthrone are retained in the new dye.



Further insight into its constitution is obtained from attempts to prepare derivatives of it from substituted pyrazole-anthrone. The presence of substituents in position 2 or 4 does not impede the formation of dyes, whereas a substituent in position 8 either inhibits the production of a dye or is removed during the process of formation. The tinctorial properties of the dye indicate that it is allied to flavanthrene. Its constitution is most pro-

bably indicated by the annexed formula, in which, however, the distribution of valencies is somewhat unusual.

Pyrazoleanthrone-yellow is most conveniently prepared in the ash-free condition by the hydrolysis of its dibenzoyl derivative with sulphuric acid. It is not affected by prolonged treatment with chromic and glacial acetic acids. When distilled with zinc dust, it gives anthracene. The following derivatives are described: *monobenzylpyrazoleanthrone-yellow*, slender, red needles; *p-chlorobenzylpyrazoleanthrone-yellow*, red needles; *o-nitrobenzylpyrazoleanthrone-yellow*, yellowish-red needles; *dibenzoylpyrazoleanthrone-yellow*, pale yellow, transparent rhombs.

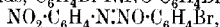
1-Chloro-2-methylanthraquinone is converted by hydrazine hydrate and a trace of iodine in boiling pyridine solution into 2-methylpyrazoleanthrone, short, yellowish-red needles, m. p. 298—300°. The latter is transformed by potassium hydroxide and alcohol into 2:2'-dimethylpyrazoleanthrone-yellow, which was not completely purified; the corresponding *dibenzyl* derivative, dark red, slender needles, and *dibenzoyl* compound, a yellow, micro-crystalline product, are described.

1-Chloro-4-methylanthraquinone is transformed by hydrazine hydrate into 1-hydrazino-4-methylanthraquinone, brownish-red needles, m. p. 185—186°, which is converted by aniline and aniline hydrochloride into 4-methylpyrazoleanthrone, slender, yellow needles, m. p. 288—290°. The latter substance yields 4:4'-dimethylpyrazoleanthrone-yellow, which is characterised as its *dibenzoyl* derivative, yellow prisms.

6-Chloro-o-2':5'-dimethylbenzoylbenzoic acid, colourless prisms, m. p. 215°, is prepared from *p*-xylene and 3-chlorophthalic anhydride in the presence of aluminium chloride and is converted by fuming sulphuric acid into 1-chloro-5:8-dimethylanthraquinone, thin yellow needles, m. p. 186°. The latter is transformed into 5:8-dimethylpyrazoleanthrone, golden-yellow leaflets, m. p. 291—292°, which could not be converted into a dye by treatment with potassium hydroxide and alcohol. On the other hand, 8-chloropyrazoleanthrone is transformed into pyrazoleanthrone-yellow. H. W.

Azoxyphenols. A. ANGELI, DINO BIGIAVI, and GINO CARRARA (*Atti R. Accad. Lincei*, 1922, [v], 31, i, 439—446).—The difference in behaviour towards oxidising agents shown by isomeric azoxyphenols (A., 1921, i, 364) resembles that observed in the action

of halogens or nitric acid on their isomeric monosubstituted derivatives. Thus, of the two para-compounds, $\text{O:NPh.N.C}_6\text{H}_4\text{Br}$ and $\text{NPh.NO.C}_6\text{H}_4\text{Br}$, only the latter readily yields the further para-substituted compounds, $\text{C}_6\text{H}_4\text{Br.N:NO.C}_6\text{H}_4\text{Br}$ and



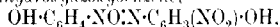
the former resisting the action of bromine or nitric acid. Hence the oxygen atom of the azoxy-group protects the aromatic nucleus united to the nitrogen atom carrying the oxygen from the action, not only of halogens or nitric acid, but also of permanganate.

Further, this protective action is exercised against nitrous acid in cold, dilute solution; in this case, one of the isomeric azoxyphenols remains unaltered, whereas the other, instead of being destroyed, is transformed into a nitro-derivative, usually easy to characterise, the structure of the original compound being thus rapidly established. Azobenzene, azoxybenzene, *p*-*z*-azoxyphenol ethyl ether, *p*-*z*-azoxyphenol, and *p*-nitrophenol are not changed when excess of sodium nitrite is gradually added to their glacial acetic acid solutions, whilst *p*-hydroxyazobenzene, *pp'*-dihydroxyazobenzene, *p*-*z*-azoxyphenol, and *pp'*-dihydroxyazoxybenzene, under the same conditions, readily yield nitro-derivatives in which the nitro-groups occupy ortho-positions with respect to the hydroxyl. For this reaction to occur, it is not sufficient for the aromatic ring to contain a hydroxyl group, it being necessary also that the hydroxylated nucleus be attached to a tervalent nitrogen atom. In the action of nitrous acid on *pp'*-dihydroxyazobenzene, the dinitro-derivative formed is accompanied by *p*-nitrophenol, the reagent acting partly as an oxidising agent; this oxidation is completely analogous to that of hyponitrous acid by permanganate when the latter acts first in an alkaline, and subsequently in an acid, solution.

3 : 3'-Dinitro-4 : 4'-dihydroxyazobenzene, obtained from *pp'*-dihydroxyazobenzene, forms lustrous, greenish-yellow needles, *m. p.* 236° (decomp.), and is probably identical with the compound, *m. p.* 240°, obtained by Robertson (T., 1913, **103**, 1473) by treating *pp'*-dihydroxyazobenzene in acetic acid solution with concentrated nitric acid.

3-Nitro-4-hydroxyazoxyphenol, $\text{O:NPh.N.C}_6\text{H}_3(\text{NO}_2)\text{OH}$, obtained from *p*-*z*-azoxyphenol, forms transparent, greenish-yellow, rhombohedral plates or green, straw-like crystals, *m. p.* 125°.

3-Nitro-4 : 4'-dihydroxyazoxybenzene,



prepared from *pp'*-dihydroxyazoxybenzene, forms lustrous, reddish-yellow needles or red, straw-like crystals, *m. p.* 193° (decomp.).

T. H. P.

The Mechanism of Coupling Reactions. II. 1 : 8-Naphthasultam and its *N*-Methyl Derivative as Azo-components. W. KÖNIG and K. KÖHLER (*Ber.*, 1922, **55**, [B], 2139—2149).—In a previous communication (A., 1921, i. 459), the power of aromatic acylamines to couple with reactive diazo-compounds with the formation of normal azo-substances has been attributed to

their ability to react in the enolic form, $\text{Ar}-\text{N}:\text{C}(\text{OH})\cdot\text{R}$ and $\text{Ar}-\text{N}:\text{SR}(\text{O})\cdot\text{OH}$. An examination of the coupling power of

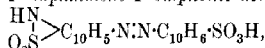
1:8-naphthasultam, $\text{C}_{10}\text{H}_6\text{SO}_2$, has shown this hypothesis to

be erroneous, since the methyl ether of this compound, $\text{C}_{10}\text{H}_6\text{SO}_2\text{Me}$, can yield normal azo-compounds in good yield. The absorption spectra of the sultam and its methyl ether prove these substances to be closely related constitutionally, and, in harmony with these observations, sodium naphthasultam is shown to stand in the same relationship to naphthasultam as does sodium α -naphthoxide to α -naphthol, so that it must be formulated $\text{C}_{10}\text{H}_6\text{SO}_2\text{Na}$ instead

of $\text{C}_{10}\text{H}_6\text{SO}_2\text{ONa}$.

The remarkable inability of *p*-toluenesulphonylmethyl- α -naphthylamide, $\text{C}_{10}\text{H}_7\text{NMeSO}_2\text{C}_6\text{H}_4\text{Me}$, to couple with diazo-compounds is explained by the assumption that the *p*-toluenesulphonyl group hinders the primary additive reaction on which coupling ultimately depends. This influence is not observed with methyl-naphthasultam in which the position of the sulphonyl group is definitely fixed, so that the nitrogen atom can exert its subsidiary valencies.

The following individual substances are described. *N*-Methyl-1:8-naphthasultam, from sodium naphthasultam and methyl sulphate in 75% yield, pale yellow needles, m. p. 125°. 4:1:8-Naphthasultamazo-1'-naphthalene-4'-sulphonic acid,



small, orange-coloured needles, decomp. 320°. 4-*p*'-Nitrobenzene-azo-1:8-naphthasultam, tile-red needles, m. p. 288–289°. 4-*op*-Dinitrobenzeneazo-1:8-naphthasultam, small, red rhombohedra with a strong pale green lustre, which darkens at 305°, but does not melt below 355°. 4-*p*-Nitrobenzeneazo-*N*-methyl-1:8-naphthasultam, $\text{NO}_2\text{C}_6\text{H}_4\text{N}:\text{N}:\text{C}_{10}\text{H}_5\text{SO}_2\text{NMe}$, lustrous, red leaflets, m. p. 236–237°. 4-*op*-Dinitrobenzeneazo-*N*-methyl-1:8-naphthasultam, m. p. 263°. 4-*op*-Dinitrobenzeneazo-1-methylaminonaphthalene-8-sulphonic acid, microscopic, red needles which have no distinct melting point. H. W.

The Alkylhydrazones. OSCAR LISLE BRADY and GERALD PATRICK McHUGH (T., 1922, 121, 1648–1652).

isoPropyl-, Menthyl-, and Bornyl-semicarbazides. Reduction of Phenylhydrazones. DE WITT NEIGHBORS, A. L. FOSTER, S. M. CLARK, J. E. MILLER, and J. R. BAILEY (*J. Amer. Chem. Soc.*, 1922, 44, 1557–1564; cf. Noyes, Lochte, and Bailey, this vol., i, 329).—Certain semicarbazones and hydrazones can be

successfully reduced by catalytic hydrogenation, whereas the older chemical methods have given only negative results.

Acetonesemicarbazone is reduced by hydrogen in the presence of colloidal platinum to *isopropylsemicarbazide*, rhombic plates, m. p. 128° (*hydrochloride*, short, stout prisms, m. p. $186\text{--}5^{\circ}$, *oxalate*, $\text{C}_6\text{H}_{13}\text{O}_5\text{N}_3$, large prisms, m. p. 172°); the yield is about 70% of that theoretically possible. A small amount of the semicarbazide is reduced further to *isopropylamine*. *isoPropylsemicarbazide hydrochloride* is transformed by sodium nitrite into the corresponding *nitroso*-derivative, short, pale yellow prisms, decomp. 128° , and by sulphuric acid (80%) into *isopropylhydrazine*, which is identified as the dibenzoyl compound, m. p. $161\text{--}5^{\circ}$. *Benzoyl-isopropylsemicarbazide*, needles, m. p. 228° , is converted by sodium hydroxide solution (30%) at 80° into *3-hydroxy-5-phenyl-1-isopropyltriazole*, prisms, m. p. $185\text{--}5^{\circ}$. Oxidation of *isopropylsemicarbazide* with potassium permanganate in alkaline solution gives acetonesemicarbazone, whereas in acid solution, *carbamylazopropane*, $\text{NPr}^i\text{N}\cdot\text{CO}\cdot\text{NH}_2$, dark yellow crystals, m. p. $65\text{--}5\text{--}66^{\circ}$, is produced (the substance is readily transformed by a trace of alkali hydroxide or by protracted exposure to the air into acetonesemicarbazone). It is probable that the azo-compound is formed immediately during the oxidation of the semicarbazide in alkaline solution.

Acetaldehydephenylhydrazone is similarly reduced to phenylethylhydrazine, $\text{NHPh}\cdot\text{NH}\cdot\text{Et}$, the yield being about 95% of that theoretically possible. It is transformed by potassium cyanate into *phenylethylsemicarbazide*, $\text{C}_9\text{H}_{13}\text{ON}_3$, microscopic needles, m. p. 138° . Acetonephenylhydrazone can be reduced similarly and with equal ease.

Menthonesemicarbazone is catalytically hydrogenated to *menthylsemicarbazide*, colourless, acicular needles, m. p. $179\text{--}180^{\circ}$, $[\alpha]_D^{20} -43\text{--}8^{\circ}$ in methyl-alcoholic solution. Similarly, camphorsemicarbazone gives *bornylsemicarbazide*, prisms, m. p. $192\text{--}5^{\circ}$, which, however, could not be converted into bornylhydrazine by the action of sulphuric acid.

H. W.

Ionising Influence of Salts with Tervalent and Quadri-valent Ions on Crystalline Egg-albumin at the Isoelectric Point. JACQUES LOEB (*J. Gen. Physiol.*, 1922, 6, 759—768).—Additional evidence in favour of the formation of ionisable salts of protein with salts containing trivalent and quadrivalent ions is afforded by the observation that lanthanum chloride and sodium ferrocyanide inhibit the heat coagulation of egg-albumin at its isoelectric point; salts containing only univalent or bivalent ions do not have this effect.

C. R. H.

Isoelectric Point of the Vegetable Albumin Leucosin. HEINRICH LÜERS and MAX LANDAUER (*Z. Elektrochem.*, 1922, 28, 341—347).—It is shown that the isoelectric point of proteins is one of the most important constants of these substances, and methods for the determination of this quantity are discussed. The isoelectric point of the vegetable albumin leucosin has been deter-

mined by five methods in an acetate buffer solution. The following values are recorded: (1) from the optimum of coagulation 2.6×10^{-5} ; (2) by cataphoresis experiments 2.8×10^{-5} ; (3) from measurements of the optimum of alcohol precipitation 2.7×10^{-5} ; (4) from measurements of the minimum of the internal friction 2.3×10^{-5} ; and (5) from the maximum of the surface tension 2.2×10^{-5} . The mean of the values gives $[H^+] = 2.5 \times 10^{-4}$, from which the relative acidity of leucosin, $k_a/k_b = 8.6 \times 10^4$. The iso-electric point of serum-, vegetable-, and yeast-albumins is thus practically the same; further, there is no noteworthy difference in the chemical composition and it is only in the biological properties that the three substances differ markedly. J. F. S.

The Physical Chemistry of the Proteins. I. The Solubility of certain Proteins at their Isoelectric Points. EDWIN JOSEPH COHN (*J. Gen. Physiol.*, 1922, 6, 697—722).—The proteins investigated were serum-globulin, tuberin, and casein. They were subjected to a rigorous process of purification, of which full details are given. After this treatment it was found that, at 25° , 1 litre of water dissolved 0.07 gram of serum-globulin, 0.1 gram of tuberin, and 0.11 gram of casein. These values were constant within wide limits of variation of the amount of protein exposed to the solvent, and are claimed to be fundamental physical characteristics which may be used in the identification of proteins.

The hydrogen-ion concentration imparted to water by the dissociated ions of the dissolved protein is also a characteristic of the protein employed. C. R. H.

The Combination of Gelatin with Hydrochloric Acid. DAVID I. HITCHCOCK (*J. Gen. Physiol.*, 1922, 6, 733—739).—The P_H was determined by hydrogen electrode measurements of 1%, 2.5%, and 5% solutions of gelatin with varying amounts of hydrochloric acid. The amounts of hydrochloric acid required to impart to pure water corresponding values of the P_H were similarly estimated. For the same P_H the difference between the total hydrochloric acid present in the first experiment and that determined by the second one represented the amount in combination with the gelatin. It was found that between P_H 1 and 2 the amount in combination is constant and amounts to 0.00092 mol. for 1 gram of gelatin. C. R. H.

The Mechanism by which Tervalent and Quadrivalent Ions Produce an Electrical Charge on Isoelectric Protein. JACQUES LOEB (*J. Gen. Physiol.*, 1922, 6, 741—757).—Direct measurements of the potential difference between originally isoelectric gelatin and solutions of various salts at P_H 4.7, with which it has been brought into equilibrium, show that a positive charge is imparted to the gelatin by a salt with trivalent cation (lanthanum chloride) and a negative charge by one with a quadrivalent anion (sodium ferrocyanide); salts containing only univalent or bivalent ions produce no charge. The effects of these salts on the osmotic pressure of solutions of isoelectric gelatin are similar to those on

the potential difference. The behaviour of lanthanum chloride towards gelatin is similar to that of an acid, whilst sodium ferrocyanide behaves like a base, and it is assumed that the effects obtained with these salts are due to the formation of complex protein-ions. Thus with lanthanum chloride there is formation of positive protein-lanthanum-ions and negative chlorine-ions; with sodium ferrocyanide of negative protein-ferrocyanide-ions and positive sodium-ions.

At P_H 3.0, when the greater part of the gelatin is ionised, solutions of lanthanum chloride have a depressing effect on the potential difference and the osmotic pressure of the solution, which is identical with that of solutions of sodium chloride and calcium chloride containing equivalent concentrations of chlorine. C. R. H.

The Influence of Aggregates on the Membrane Potentials and Osmotic Pressure of Protein Solutions. JACQUES LOEB (*J. Gen. Physiol.*, 1922, 6, 769—776).—The potential difference between a solution of gelatin chloride in a collodion bag and an outside aqueous solution is practically unaffected if, at the same P_H , part of the gelatin in solution is replaced by powdered gelatin; moreover, the membrane potential can be calculated from the differences in P_H inside and outside the bag, which shows that the gelatin particles take part in the establishment of the membrane equilibrium. On the other hand, the osmotic pressure of a gelatin chloride solution is progressively lowered as the gelatin in solution is replaced by powdered gelatin, showing that the particles of gelatin do not participate in the production of the osmotic pressure of the solution. This is explained by the fact that, since each particle is subject to the conditions of the Donnan equilibrium, a special osmotic pressure is set up in each particle which is balanced by an increase in the cohesion pressure of the particles, and does not therefore manifest itself in the hydrostatic pressure by which the osmotic pressure of the solution is measured; it is due to the gelatin in true solution alone. C. R. H.

The Hydroxyproteic Acids. S. EDLBACHER (*Z. physiol. Chem.*, 1922, 121, 164; cf. this vol., i, 692).—The compound $C_{16}H_{18}O_2N_4$ described by the author (*loc. cit.*) is apparently acetylphenylhydrazine. W. O. K.

The Absorption Spectra of Methæmoglobin, and the Alleged Transformation of Methæmoglobin into Oxyhæmoglobin by the Action of Alkali. G. QUAGLIARIELLO (*Arch. Sci. biol.*, 1922, 3, 65—86; from *Physiol. Abstr.*, 1922, 7, 215).—Neutral methæmoglobin has four absorption bands, at λ 631 $\mu\mu$, λ 576 $\mu\mu$, λ 540 $\mu\mu$, and λ 500 $\mu\mu$. Alkaline methæmoglobin has three absorption bands; the first at λ 600 $\mu\mu$; the other two are in the same place as the second and third of neutral methæmoglobin. The absorption bands in the yellow and green are proper to methæmoglobin, and not due to the presence of oxyhæmoglobin. A transformation of methæmoglobin into oxyhæmoglobin through the action of hydroxyl ions is excluded. W. O. K.

The Prosthetic Group of the Blood Pigments. Hæmatin. WILLIAM KÜSTER (*Z. physiol. Chem.*, 1922, 121, 121—134).—*Bromodimethylhæmin*, $C_{36}H_{36}O_3N_4BrFe$, small needles, is prepared from the part of a crude β -hæmin insoluble in chloroform, by boiling with methyl alcohol containing sulphuric acid, and precipitating with 66% hydrobromic acid. Although chlorine cannot be quantitatively eliminated from chlorodimethylhæmin by methyl alcoholic potash without causing hydrolysis, the bromo-compound can be dehalogenated completely, to form a *dimethylhæmatin*, $C_{36}H_{36}O_4N_4Fe \cdot OH \cdot H_2O$, a dark-coloured compound with a metallic lustre. If this be treated with sodium hydroxide solution at the room temperature, not only does hydrolysis take place, but water is also eliminated. This bears out the view that in the formation of hæmatin from hæmin the bond between the iron and a nitrogen atom is hydrolysed, and that the iron then forms an internal salt with a carboxyl group, eliminating water. If, as in this instance, the carboxyl group is first methylated, the internal salt cannot be formed until the ester is hydrolysed.

Treatment of bromodimethylhæmin with pyridine leads to simple replacement of bromine by hydroxyl, forming *hydroxydimethylhæmin*, $C_{36}H_{36}O_4N_4Fe \cdot OH$, from which a bromodimethylhæmin can be regenerated by treating it in acetone solution with hydrogen bromide solution, although the absolute identity of the compound formed with the initial bromodimethylhæmin is not yet certain.

A particular preparation of hæmatin, obtained from hæmin and de(hydrohalogen)hæmin, was found to be readily methylated by methyl sulphate and alkali to yield a *dimethylhæmatin*, $C_{36}H_{37}O_3N_4Fe$, as an amorphous, dark blue, metallic compound, which with alkali loses a methyl group to form a *monomethyl* derivative, $C_{35}H_{35}O_3N_4Fe$. This dimethylhæmatin was further methylated by boiling with methyl alcohol containing sulphuric acid, and then treating with 66% hydrobromic acid, when a *bromodimethylhæminium trimethobromide*, with the formula $C_{34}H_{30}O_2N(NMeBr)_3(OMe)_2FeBr$, is precipitated, indicating the presence of three basic nitrogen atoms in hæmatin. This new compound is more completely demethylated with alkali than dimethylhæmatin itself, pointing to the opening of the bond between nitrogen and iron on boiling in acid solution. Preparations of hæmatin from formylhydroxylhæmin or from chlorodimethylhæmin were not methylated in a similar manner. In the first case, the compound finally obtained had the formula $C_{39}H_{48}O_7N_4BrFe$.

W. O. K.

Hæmocyanin. VI and VII. C. DHÉRE and A. SCHNEIDER (*J. Physiol. Pathol. gén.*, 1922, 20, 1—13, 34—40; from *Physiol. Abstr.*, 1922, 7, 218).—Oxyhæmocyanin of *Helix*, *Octopus*, *Homarus*, etc., is easily and rapidly reduced by the passage of inert gas at 15° to 20°, or by exposure to a vacuum at 40°. The solutions were made of pure crystallised preparations, and usually in presence of an antiseptic. The gas must be absolutely deprived of oxygen. The hæmocyanin of *Limulus* may be different. That of the above

animals forms a less dissociable compound with nitrous oxide, but not with methane, ethylene, or acetylene. It does not combine with carbon monoxide, or if it does the compound is very easily dissociable.

W. O. K.

Bile Pigments. XI. The Preparation and Purification of Bilirubin from Ox Gallstones. WILLIAM KÜSTER (*Z. physiol. Chem.*, 1922, **121**, 80—93).—Experiments are described on the preparation and purification of bilirubin from ox gallstones. It is found convenient to isolate the bilirubin in the form of its crystalline compound with ammonia, $C_{33}H_{36}O_6N_4 \cdot NH_3$.

The statement of Reihling (*A.*, 1915, **1**, 831) that choleprasin yields hæmatic acid on oxidation is apparently to be explained by the presence of some bilirubin in the choleprasin. W. O. K.

Bile Pigments. XII. The Action of Diazomethane on Bilirubin and Biliverdin, the Oxidation of Bilirubin in Alkaline Solution, and the Action of Hydrogen Bromide-Acetic Acid on Bilirubin. WILLIAM KÜSTER (*Z. physiol. Chem.*, 1922, **121**, 94—109).—By treating crude bilirubin, $C_{33}H_{36}O_6N_4$, with diazomethane in ethereal solution, two methyl groups enter the molecule and in addition a molecule of diazomethane is combined, forming a compound, $C_{35}H_{42}O_6N_6$, which on heating loses nitrogen to form the compound $C_{35}H_{42}O_6N_4$. Using bilirubin-ammonia in the methylation, the ammonia group is retained, and a compound, $C_{35}H_{45}O_6N_7$, formed, a dark brown, resinous material, which also loses nitrogen when heated, forming the compound $C_{35}H_{45}O_6N_5$.

Biliverdin, $C_{33}H_{36}O_8N_4$, obtained by the atmospheric oxidation of bilirubin in alkaline solution, forms with alcoholic hydrogen chloride a dimethyl ester, $C_{35}H_{40}O_8N_4$, a dark, lustrous material, and with diazomethane a dimethyl ester of similar composition, although it is not certain whether the preparations are identical.

Bilirubin-ammonia, on long-continued action of alkali hydroxide, and exposure to the air with stirring, yields hæmatic acid and an acid, $C_7H_{10}O_5$ (barium salt, $C_7H_8O_5Ba$; silver salt, $C_7H_8O_5Ag_2$), which may be a methylhydroxyethylmaleic acid.

Treatment with hydrogen bromide-acetic acid and then with water converts bilirubin-ammonia into the compound $C_{33}H_{34}O_8N_4Br$, which on treatment with 10% sodium hydroxide solution loses bromine to form the compound $C_{33}H_{32}O_8N_4$. If the material from the treatment with hydrogen bromide-acetic acid be treated with methyl alcohol instead of with water, the compound

$C_{33}H_{35}O_4N_4Br(OMe)_2$ is obtained, which also loses bromine on treatment with sodium hydroxide solution.

Sometimes the reaction with hydrogen bromide-acetic acid, followed by treatment with water proceeds differently, and a compound, $C_{33}H_{36}O_8N_4Br$, is formed which on oxidation forms hæmatic acid, and on reduction hæmatic acid and the imide of methyl-ethylmaleic acid.

W. O. K.

Bile Pigments. XIII. Hexachlororubilic Acid. WILLIAM KÜSTER and WALTER HERRMANN (*Z. physiol. Chem.*, 1922, **121**, 110—120).—By treatment of bilirubin with a mixture of Merck's perhydrol and concentrated hydrochloric acid, *hexachlororubilic acid* is formed, a light yellow powder which, after thorough desiccation, decomposes at about 80°, and has the formula $C_{18}H_{23}O_6N_3Cl_6$. It is a dibasic acid forming a *monomethyl ester*, $C_{19}H_{23}O_6N_2Cl_6$, a citron-yellow powder, on dissolving in methyl alcohol, saturating with hydrogen chloride, and keeping cooled with ice, whilst if the methyl alcohol solution is boiled after saturating with hydrogen chloride, the *dimethyl ester* is formed, which on treatment with sodium hydroxide solution yields the *dimethyl ester* of penta-chlorohydroxyrubilic acid, $C_{20}H_{25}O_7N_2Cl_5$. Sodium hydroxide solution removes one of the chlorine atoms from hexachlororubilic acid, forming *pentachlorohydroxyrubilic acid*, $C_{18}H_{21}O_7N_2Cl_5$. Hexachlororubilic acid loses hydrogen chloride slowly on keeping, more quickly on heating in a vacuum, to form a *compound*, $C_{18}H_{19}O_6N_3Cl_5$. With sulphuric acid, it reacts to yield a *compound*, $C_{18}H_{18}O_5N_3Cl_6$, by elimination of water, and with gaseous ammonia it forms the *compound* $C_{18}H_{23}O_6N_3Cl_6$. W. O. K.

Degree of Dispersion of Saccharase. H. VON EULER and GÖRAN ERICSON (*Kolloid Z.*, 1922, **31**, 3—7).—A number of diffusion experiments with highly purified yeast saccharase solutions are described from which calculations of the molecular weight of the saccharase particle have been made by means of the formula $D\sqrt{M}=\text{const.}$ The saccharase solutions were purified by a combination of the methods previously used by Willstätter and Racke (A., 1921, i, 823; this vol., i, 598) and the older precipitation methods. In this way, the albuminous substances and yeast gums have been removed and the purity of the saccharase solution increased in the proportion 1:20. The purest material gives an average molecular weight of 20,000 as compared with the values 27,000 and 22,000 found by Euler and Kullberg (A., 1911, i, 825) and Euler, Hedelius, and Svanberg (A., 1921, ii, 170; 1920, ii, 595), respectively. J. F. S.

Influence of Various Antiseptics on the Activity of Lipase. LEROY S. PALMER (*J. Amer. Chem. Soc.*, 1922, **44**, 1527—1538).—Data are presented on the influence of various concentrations of several antiseptics on the hydrolysis of emulsions of milk fat in gum acacia solutions, using commercial steapsin as the source of lipase.

Formaldehyde in concentrations up to one part in two hundred and fifty parts had no detrimental effect on the activity of the lipase, 1% solutions being required to produce a retardation of the enzyme. Chloroform in concentrations from 1.5 to 2.5% retarded the lipase activity from 20 to 60%. Acetone in concentrations of 6% and 12% retarded the lipolysis 12% to 25%. A freshly prepared 3% solution of iodoform in acetone added so as to give a concentration of 0.3% of iodoform retards the lipase action 25% to 40%. When using a similar solution of iodoform,

which had stood for some time, practically complete inhibition was obtained with this and even smaller concentrations of iodoform. In the experimental examination of these results, it was found that iodoform alone retarded lipolysis in direct proportion to the concentration of the iodoform present. This varied from a 15% retardation with 0.03% concentration of iodoform to a 55% retardation with 0.5% concentration of the antiseptic. It was found, also, that old solutions of iodoform in acetone contain free iodine, which has a marked effect on lipase activity. Iodine, in concentrations of 0.045% or more, inhibited lipolysis entirely. Results similar to those with iodine were obtained by the use of bromine water. Higher concentrations of bromine were found necessary to inhibit the lipase, however, concentrations of 0.25% retarding the enzyme activity only 93% to 94%. Mercuric chloride inhibited lipase activity completely in 0.1, 0.2, and 0.3% concentrations. Chloral hydrate not only retarded the lipase, but also failed as a germicide when cow's milk was used as substrate.

The results obtained with the halogens appear to indicate that lipase has an unsaturated structure which is probably aliphatic rather than cyclic. This suggestion is supported by the results on the failure of formaldehyde to retard lipase even in fairly high concentrations.

H. W.

Periodicity of Enzymes. The Lipase of the Stomach. E. SLUTER (*Nederland Tijdschr. Geneeskunde*, 1922, **66**, 572).—The activity of a solution of lipase, prepared from mucous membranes, and kept in an ice-chest, was determined daily by shaking with an equal volume of milk for twenty-four hours at 37° and titrating the free fatty acid with 0.1N-alkali solution. Whether or not the preparation is kept slightly acid, the activity is found to change irregularly in periods of several days. It is not considered that such variations play any part in vivo.

CHEMICAL ABSTRACTS.

Action of Quinine and Atoxyl on Liver Lipase. P. RONA and R. PAVLOVIĆ (*Biochem. Z.*, 1922, **130**, 225—238).—Although liver lipase and serum lipase act identically on tributyrin, liver lipase is not influenced detrimentally by quinine in concentrations which far exceed those which completely inhibit the action of serum lipase. Liver lipase is, however, more sensitive to atoxyl than serum lipase. In the case of both lipases, the velocity constants for the hydrolysis of tributyrin fall off in arithmetical progression as the concentrations of toxic substances are raised in geometrical progression.

H. K.

Isolation of Vitamin. A. SELDELL (*Abstr. of Bacteriol.*, 1922, **6**, Proc., 101; from *Physiol. Abstr.*, 1922, **7**, 245—246).—An aqueous solution of vitamin is prepared from brewer's yeast by suspending in water and heating at about 90° for several minutes. The coagulated protein is removed and fuller's earth added to the clear solution. The fuller's earth, which selectively adsorbs the vitamin, is filtered, washed, and dried, and designated "activated

solid." The vitamin is most conveniently recovered from the activated solid by rapidly extracting with saturated barium hydroxide solution and acidifying the clear extract with sulphuric acid. Addition of solid barium carbonate removes the excess of acid. The filtered neutral solution is then evaporated and yields a crude extract which will protect pigeons when fed exclusively on polished rice in doses of about 10 mg. every other day. The vitamin extract was subjected to fractionation by silver precipitation, and it was found that a small amount of adenine was present and a larger amount of histidine. The characteristic vitamin action always accompanied the histidine fraction, and it appears possible that either vitamin is a derivative of histidine, or it is a compound of similar chemical properties which accompanies the histidine as an impurity. It was found that when the silver was removed from the histidine-silver precipitate by suspension in dilute hydrochloric acid, the clear solution could be evaporated to dryness on the steam-bath without appreciable impairment of its vitamin activity. The residue so obtained was found to protect pigeons on a diet of polished rice in doses of less than 1 mg. every other day.

W. O. K.

Arsenical Acridine Compound. L. BENDA (U.S. Pat. 1408974). The diazo-compound of 3:6-diamino-10-methylacridinium chloride is treated with sodium arsenite, producing a reddish-brown powder which combines with R salt to produce a red compound and with resorcinol to produce an orange-yellow product. The compound is of low toxicity and its use medicinally is proposed.

CHEMICAL ABSTRACTS.

Organic Mercury Compounds prepared from o-Chloromercuri-p-nitrobenzoyl Chloride. FRANK C. WHITMORE and EDMUND BURRUS MIDDLETON (*J. Amer. Chem. Soc.*, 1922, **44**, 1546—1551).—Phosphorus pentachloride can be used as well as thionyl chloride in the preparation of acid chlorides of mercurated aromatic acid. o-Chloromercuri-p-nitrobenzoyl chloride has been obtained in this manner and converted into a number of its esters. The latter compounds react with inorganic iodides to form the corresponding compounds of the type R_2Hg ; these substances can be hydrolysed without breaking the C-Hg linking.

o-Hydroxymercuri-p-nitrobenzoic acid, prepared by heating mercuric p-nitrobenzoate at 200–220°, is converted by phosphorus pentachloride in the presence of chloroform into o-chloromercuri-p-nitrobenzoyl chloride, which could only be obtained with difficulty in the analytically pure condition. It is transformed by the requisite alcohol into the n-butyl ester, m. p. 125–126°; n-propyl ester, m. p. 145–150°; isopropyl ester, m. p. 179–180°; ethyl ester, m. p. 220–222°; methyl ester, m. p. 240–245°, and chloroethyl ester, m. p. 163–164°. The acid chloride reacts readily with ethylene bromohydrin and diethylaminoethyl alcohol, but a homogeneous product could not be isolated. The position of the mercury complex in the esters is established by the observation that they are converted by cold bromine water and subsequent hydrolysis

into *o*-bromo-*p*-nitrobenzoic acid. *o*-Chloromercuri-*p*-nitrobenzanilide is described.

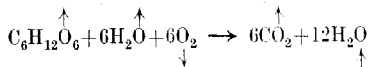
Butyl *o*-chloromercuri-*p*-nitrobenzoate is converted by potassium iodide in boiling ethyl alcoholic solution into *n*-butyl *o*-mercuribis-*p*-nitrobenzoate, $\text{Hg}(\text{C}_6\text{H}_4[\text{NO}_2])\cdot(\text{CO}_2\text{C}_4\text{H}_9)_2$, colourless crystals, m. p. 158° ; the compound is converted by a boiling ethyl alcoholic solution of mercuric chloride into butyl *o*-chloromercuri-*p*-nitrobenzoate, m. p. 125° , and by ethyl alcoholic sodium hydroxide solution into *o*-mercuribis-*p*-nitrobenzoic acid. The corresponding *n*-propyl ester, m. p. 189° , and ethyl ester, m. p. $227\text{--}232^\circ$, are described.

n-Butyl *o*-chloromercuribenzoate, m. p. 115° , is prepared by the successive action of phosphorus pentachloride (or thionyl chloride) and *n*-butyl alcohol on *o*-hydroxymereuribenzoic anhydride.

H. W.

Physiological Chemistry.

Is there a Genetic Relation between the Oxygen Inhaled and the Oxygen of the Exhaled Carbon Dioxide? TORSTEN THUNBERG (*Naturwiss.*, 1922, **10**, 417—420).—Hydrogen is regarded as the basic, elementary combustible of living cells; it is supposed to be directly oxidisable by oxygen at low temperatures, in consequence of activation by catalysts. Decomposition of complex compounds occurs by enzyme action through a series of progressive dehydrogenations, the hydrogen eliminated being directly oxidised to water; at the same time, there is addition of water and elimination of carbon dioxide. It is contended that there is no relation between inhaled oxygen and exhaled carbon dioxide; this is represented, for example, by the scheme:



(cf. Dixon, T., 1886, **49**, 94; Wartenberg and Sieg, A., 1921, ii, 107).
(CHEMICAL ABSTRACTS.)

Anæsthetics and Carbon Dioxide Output. I. The Effect of Anæsthetics and Other Substances on the Production of Carbon Dioxide by certain Orthoptera. J. H. BODINE (*J. Expt. Zool.*, 1922, **35**, 323—334).—Ethyl ether (in large doses), acetone, xylene, and formaldehyde produce an increase in carbon dioxide output, followed by a decrease which is irreversible. Chloroform causes a decrease followed by an increase and later by a decrease, the change being irreversible. With small doses of acetone, the increase extends over a long period of time; with large doses it is short-lived; the decrease is to a rate of carbon dioxide output still above normal. With formaldehyde, the

decrease is to the normal rate, but with large doses it is below normal. Ethyl ether, chloroform, acetone, and xylene inhibit respiratory movements in ten to fifteen minutes; formaldehyde in relatively large doses does not inhibit these movements in two hours. These results show that narcosis is not due to asphyxia. Anaesthetics have an action other than that on respiration. Grass. Hoppers of several species were used in these experiments.

CHEMICAL ABSTRACTS.

Respiratory Metabolism in Alimentary Glycæmia. I. A. BORNSTEIN and KURT HOLM (*Biochem. Z.*, 1922, **130**, 209—224).—In a fasting man oral administration of 100 grams of dextrose causes the blood-sugar content to rise progressively after a few minutes, but respiratory experiments show that the combustion of the dextrose only sets in about half an hour later, often after the blood-sugar has reached or passed its maximum value. When, however, 100 grams of levulose are administered, the blood-sugar scarcely rises at all, owing to immediate combustion of sugar. Phosphate administration has no influence, but it is thought that the dextrose must first pass into levulose or a closely related substance before combustion.

H. K.

Direct Measurement of the Partial Pressure of Oxygen in Human Blood. J. BARCROFT and M. NAGAHASHI (*J. Physiol.*, 1921, **55**, 339—345).—The principle of the method is as follows: Blood is withdrawn from a vessel, artery, or vein, by direct puncture; to this blood is exposed a small bubble of alveolar air at 37° until an equilibrium is reached between the blood and the bubble. The bubble is then analysed in a suitable apparatus. The original must be consulted for details. Oxygen pressure in blood can be measured to within 2 mm. on the average. The calculated dissociation curves for venous blood were experimentally confirmed. The observation of Meakins and Davies (*J. Path. Bact.*, 1920, **23**, 451) on the great range of unsaturation of blood from the basilar vein when the arm is exposed to widely differing temperatures was confirmed.

CHEMICAL ABSTRACTS.

Acid Production in Shed Blood. C. L. EVANS (*J. Physiol.*, 1922, **56**, 146—156; from *Physiol. Abstr.*, 1922, **7**, 233—234).—The carbon dioxide capacity of blood is at its highest level in freshly-drawn blood, and usually suffers considerable reduction when the blood is kept. The change is due to conversion of dextrose into lactic acid as a result of glycolysis; it is greatly accelerated by a lowering of the carbon dioxide pressure of the blood, because this gives a P_{11} favourable to the glycolytic process. These facts are of importance in the plotting of carbon dioxide dissociation curves. When blood-gas phase equilibration is to be carried out at body temperature, the glycolytic change, with its accompaniment of reduction of carbon dioxide capacity, can be inhibited by the addition of 0.05 to 0.1% of sodium fluoride to the blood.

W. O. K.

The Hydrogen-ion Concentration and some Related Properties of Normal Human Blood. J. BARCROFT, A. V. BOCK, A. V. HILL, T. R. PARSONS, W. PARSONS, and R. SHOJI (*J. Physiol.*, 1922, **56**, 157—178; from *Physiol. Abstr.*, 1922, **7**, 233).—Between 20 and 40 mm. pressure of carbon dioxide, the relation between the P_{H_2} in the plasma and the pressure of carbon dioxide (pCO_2) is nearly linear. So also is that for the relation between pCO_2 and vCO_2 (volume of carbon dioxide absorbed), the empirical expression being $P_{H_2}=4.7pCO_2/vCO_2$. Hence the relation between P_{H_2} and vCO_2 is also linear, and is expressed by the formula $vCO_2=b(10^8P_{H_2})+c$, where $b=8.4\pm 2$ and $c=16.6\pm 10$. The quantity b is a measure of the buffering power of the blood; that is, it expresses the slope of the vCO_2 - P_{H_2} curve. The relation between $1/K$ and pCO_2 is not quite linear but slightly S-shaped (K is the constant of Hill's oxygen dissociation equation), although the relation between $\log 1/K$ and $\log P_{H_2}$ is linear. W. O. K.

The Comparative Blood-pressure raising Power of Racemic and Lævo-Adrenaline. A. RICHAUD (*J. Pharm. Chim.*, 1922, [vii], **26**, 81—86).—*r*-Adrenaline employed in very small doses of the order of 0.01 mg. increases the blood pressure to a somewhat lesser degree than *l*-adrenaline, but the difference in activity is not by any means so great as has been supposed. It is not constant, but varies from 10—15% in general, although it may be as much as 25—30%. As the dose is increased to 0.04—0.05 mg. the difference in activity disappears entirely, and as the usual therapeutic dose is 0.04—0.1 mg. there is no disadvantage attendant on the use of the racemic compound, and the resolution of the synthetic substance into its optical isomerides is therefore quite unnecessary. G. F. M.

Condition of Electrolytes in the Blood. BENJAMIN S. NEUHAUSEN (*Nature*, 1922, **110**, 8—9).—*E.M.F.* measurements of serum and plasma were made, using 0.2% sodium amalgam as a sodium electrode. Calculation of the total concentrations of sodium on the basis that the degree of ionisation of the sodium salts was the same as in an aqueous solution, gave results which were in very good agreement with those found by analysis. Thus the conclusions of other investigators that sodium is not bound in the serum have been confirmed. Chlorine likewise is apparently as free as in an aqueous solution. A silver/silver chloride electrode was used for these experiments. It is proposed to use a calcium electrode to determine the state of calcium in the blood. A. A. E.

The Calcium in the Blood in Different Species. P. MAZZOCCO (*Compt. rend. Soc. Biol.*, 1921, **85**, 690—691; from *Chem. Zentr.*, 1922, i, 209; cf. *A.*, i, 788).—The calcium content of the total blood and of individual blood constituents for a number of different animal species is given. The calcium content of blood corpuscles was found to be the same in citrated blood and in blood treated with hirudin. G. W. R.

Influence of Water Supply on the Content of Reducing Substances in the Blood and Urine. A. NORGAARD (*Biochem. Z.*, 1922, **130**, 304—311).—Administration of a litre of water to fasting persons has little effect on the amount of reducing substances in the blood. In the urine, the reducing substances fall off considerably during the increased diuresis, but the actual quantity of reducing substances excreted is not affected. H. K.

The Action of Heterogeneous Proteins in the Organism. A. LÜTTICHAU (*Arch. int. physiol.*, 1922, **19**, 1—16).—The effect on the blood-sugar was investigated of intravenous injection into dogs of solutions or suspensions of egg-albumin, egg-globulin, human saliva, casein, horse-serum, gelatin, ascitic fluid, and Witte's peptone. The ova-proteins, salivary proteins, and casein produced hyperglycæmia, but not glycosuria; the effect of egg-white is due to its globulin content. None of the substances used, except saliva, had any diastatic action on glycogen in vitro. The phenomenon is considered as probably a glucose mobilisation.

CHEMICAL ABSTRACTS.

The Inhibition of Blood Coagulation by Barium, Strontium, and Calcium Chlorides. JÖRGEN LEHMANN (*Skand. Arch. Physiol.*, 1922, **42**, 35—42; from *Chem. Zentr.*, 1922, i, 597).—When blood is mixed with half its volume of barium chloride solution so that the concentration in the mixture is 0.07%, coagulation is inhibited. Calcium has a weaker, and strontium a still weaker effect. G. W. R.

The Reaction of Blood. RUTH E. CONWAY and FLORENCE V. STEPHEN (*J. Physiol.*, 1922, **56**, Proc., xxv—xxvii; from *Physiol. Abstr.*, 1922, **7**, 233).—The inside of the blood-corpuscle is about 35% more acid than the outside. The basic ion concentration is considerably greater in the serum than in the corpuscle. The buffering of laked blood is less efficient than that of unlaked. Cases of pernicious or severe secondary anæmia show an alteration in buffering in direct relation to the percentage of hæmoglobin present. W. O. K.

Calcium Content of Blood Serum in Pregnancy and Childbirth. P. MAZZOCCO and R. BUSTOS MORÓN (*Compt. rend. Soc. Biol.*, 1921, **85**, 692; from *Chem. Zentr.*, 1922, i, 209—210).—The calcium content of the blood-serum in pregnancy and childbirth is only slightly below normal, namely, 8.77—8.79 mg. per 100 c.c. as against 9.19 mg. per 100 c.c. in normal sera. The calcium content of the serum is thus of no diagnostic value for pregnancy. No correlation can be shown between the fall in serum calcium and the development of pregnancy and its related maladies. G. W. R.

Eosin Hæmolysis. CARL L. A. SCHMIDT and G. F. NORMAN (*J. Gen. Physiol.*, 1922, **6**, 681—687).—The hæmolysis of red blood cells which takes place on exposure to sunlight in the presence of eosin is inhibited by inorganic reducing agents and certain easily

oxidisable substances such as tyrosine, tryptophan, and other substances which react with the phosphotungstic reagent of Folin and Denis. It is assumed that the hæmolytic action of cosin involves the oxidation of the tyrosine and tryptophan which are contained in the stroma of the cells.

C. R. H.

The Digestibility of Proteins in Vitro. III. The Chemical Nature of the Nutritional Deficiencies of Arachin. D. BREESE JONES and HENRY C. WATERMAN (*J. Biol. Chem.*, 1922, **52**, 357—366).—Arachin is less readily digested in vitro by pepsin and trypsin than, for example, casein. Hydrolysis by hot, dilute sodium hydroxide yields a partial cleavage product which represents about one-third of the original arachin. This product is difficultly digestible in vitro and contains about two-thirds of the histidine, one-third of the arginine and of the cystine, and two-fifths of the lysine present in the arachin from which it was prepared. Further work is necessary to determine if the nutritional inadequacy of the protein is due to this factor.

E. S.

Carbohydrate Metabolism and Diabetes. IV. Dextrose-Nitrogen Ratios in Partially Depancreatized Dogs. F. M. ALLEN and MARY B. WISHART (*J. Metabolic Res.*, 1922, **1**, 97—107; cf. *J. Biol. Chem.*, 1920, **42**, 415; 1920, **44**, 563).—Total pancreatectomy does not invariably give rise to a permanent "total" dextrose:nitrogen ratio of 2.8:1, whilst incompletely depancreatized animals sometimes show this, and sometimes a lower ratio. The total basal metabolism, and the loss of both sugar and nitrogen are higher in the case of totally depancreatized animals, the former partly in consequence of greater protein breakdown.

CHEMICAL ABSTRACTS.

The Threshold of Ketogenesis. RUSSELL M. WILDER and MALCOLM D. WINTER (*J. Biol. Chem.*, 1922, **52**, 393—401).—From calculations, based on a number of assumptions, of the composition of the food being metabolised in certain cases, it is concluded that the molecular ratio of ketogenic substance to dextrose at which significant ketosis first appears is 2:1. This ratio, which is termed the ketogenic threshold, is lowered by infection and possibly also by other factors (cf. Shaffer, A., 1921, i, 754; Hubbard and Wright, this vol., i, 496).

E. S.

The Importance of Zinc in the Feeding of Animals. Experiments on Mice. GABRIEL BERTRAND and B. BENZON (*Compt. rend.*, 1922, **175**, 289—292).—The lives of mice fed on a specially prepared food containing an amount of zinc sulphate equivalent to 0.002% Zn were prolonged from 25—50% beyond those of animals from the same litter fed on the same food prepared absolutely free from zinc.

G. F. M.

The Measurement of Buffer Values and the Relationship of Buffer Value to the Dissociation Constant of the Buffer and the Concentration and Reaction of the Buffer Solution. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1922, **52**, 525—570).—A theoretical paper, the object of which is to give quantitative

expression to buffer effects. For this purpose, the buffer value, β , of a solution is defined as the number of gram equivalents of strong alkali or acid which must be added (strictly without change of volume) to one litre to produce unit change in P_H . Formulated mathematically, $\beta = dP/dP_H$ (cf. Koppel and Spiro, A., 1914, i, 1105, who have given a somewhat similar definition). An increment of strong acid is regarded as a negative increment of strong base; hence the value of β is always positive. Starting from the laws of ionic mass reaction, the following general equation for buffer value has been deduced: $\beta = 2.3(K'[H']C)/(K' + [H']^2 + [H'] + [OH'])$, in which K' represents either K_a/γ_a or K_b/γ_b , according as the buffer is a weak acid or a weak base, and C is the molecular concentration of buffer acid (or base). When the P_H is between 3 and 11 and C is not much less than 0.1N, $[H']$ and $[OH']$ may be neglected and the equation simplifies to $\beta = 2.3K'[H']C/(K' + [H']^2)$, an expression which has also been deduced directly from Henderson's equation: $K_a = [H']_a[Ba]/[Ha]$. Under these conditions, $\beta/C (= \beta_M) = 2.3K'[H']/(K' + [H']^2)$, β_M being termed the molecular buffer value of the buffer acid or base. By differentiation of the last equation, it is shown that the maximum value of β_M occurs when $[H'] = K'$, and it follows that at this point $\beta_M = 2.3/4 = 0.575$ for all buffers. Further, when $K' = [H']$, $[H] = [Ba]$; hence at the maximum molecular buffer value half the buffer acid (or base) is present in the free state and half in the form of salt. The above methods have been extended to the calculation of β for solutions of multivalent, amphoteric, and mixed buffers. E. S.

The Relationship of Odour to Molecular Structure. RAYMOND DELANGE (*Bull. Soc. chim.*, 1922, [iv], 33, 589—630).—Report of a lecture. An extensive bibliography is appended. H. J. E.

Odour Value Analysis. W. G. UNGERER and R. B. STODDARD (*Ungerer's Bull.*, 1922, 3, 7—10).—It is suggested that odour is the response of the olfactory nerves to intermolecular vibrations, of a magnitude such that they can scarcely be detected. Every pure substance is assumed to have a specific rate of vibration, which may or may not be within those limits which produce the sensation of odour. Support is claimed for this theory from the fact that practically all substances having a perceptible odour are chemically unsaturated. The conception also explains the effect of impurities of characteristic but not powerful odour in modifying to a profound degree the odour of other substances which, in a pure state, may become almost odourless. CHEMICAL ABSTRACTS.

Chemical Composition of Amniotic Fluid. A. LABAT and M. FAVREAU (*J. méd. Bordeaux*, 1921, 92, 341—342; from *Chem. Zentr.*, 1922, i, 210; cf. Uyeno, A., 1920, i, 201—202).—The authors give the following data for the composition of amniotic fluid: dry matter, 13.30%; organic matter, 6.56%; ash, 6.81%; sodium chloride, 5.25%; protein, 2.40%; urea, 0.28%. Dextrose was found occasionally in small quantities. An increase in dry matter, salts, and protein is, found during pregnancy. G. W. R.

Quantity of Combined Carbonic Acid in Cerebrospinal Fluid. E. TOKUOKA and K. OGASAWARA (*Japan Med. World*, 1921, 1, 6; *J. Amer. Med. Assoc.*, 78, 387).—In the spinal fluid of healthy women the combined carbon dioxide averaged 63 vol. %. In the venous blood the carbon dioxide averaged 54.4 vol. %, and is decreased after starvation. In cancerous women, the carbon dioxide was about 3 vol. % in the spinal fluid and 4.7 vol. % less in the blood than in normal women.

CHEMICAL ABSTRACTS.

The Influence of the Concentration of Sugar on the Synthesis of Glycogen. STEFAN ÉDERER (*Biochem. Z.*, 1922, 130, 294—298).—Experiments, in vitro, with dog's liver pulp, on the change of glycogen content with time in presence of various concentrations of dextrose show that glycogen disappears. The fall of glycogen content is inhibited to a large extent by addition of sodium oleate. The glycogen-dextrose balance in the blood is therefore not governed by the law of mass action. H. K.

Unsataponifiable Constituents (Higher Alcohols) of Shark and Rayfish Liver Oils. II. YOSHIYUKI TOYAMA (*Chem. Umschau*, 1922, 29, 237—240, 245—247; cf. Tsujimoto and Toyama, this vol., i, 297).—The liver oil of *Chlamydoselachus anguineus* gave the following constants: d_4^{20} 0.8747—0.8885; acid number, 0.23—0.66; saponification number, 93.4—116.5; iodine number (Wijs), 112.1—136.3; n_D^{20} 1.4703—1.4725; unsaponifiable substances, 37.06—51.65%; acid number of the fatty acids, 182.8—189.8; iodine number of the fatty acids, 77.6—99.7; polybromide number of the fatty acids, 4.80—5.58. The principal constituent of the unsaponifiable substances is oleic alcohol. Squalene is also present together with small amounts of cetyl alcohol and cholesterol.

The oil from the liver of *Scymnorhinus licha* has d_4^{20} 0.8890; acid number, 0.20; saponification number, 98.1; iodine number, 191.5; n_D^{20} 1.4791; unsaponifiable substances, 48.51%. It contains 30% of squalene and selachyl and batyl alcohols.

Oil from the liver of *Centrosyllium Ritteri* has d_4^{20} 0.8917; acid number, 5.10; saponification number, 92.1; iodine number, 213.7; n_D^{20} 1.4812; unsaponifiable substances, 53.06%. The unsaponifiable substances contain squalene, selachyl, and batyl alcohols.

Oil from the liver of *Galocerdo tigrinus* has d_4^{20} 0.9108; acid number, 0.26; saponification number, 174.0; iodine number, 75.2; n_D^{20} 1.4680; unsaponifiable substances, 11.48%, consisting almost entirely of selachyl and batyl alcohols.

Oil from the liver of *Heptranchias deani* has d_4^{20} 0.9162; acid number, 0.36; saponification number, 174.9; iodine number, 118.5; n_D^{20} 1.4734; unsaponifiable substances, 12.68%, consisting principally of selachyl and batyl alcohols.

Oil from the liver of *Centrophorus sp.* contains 49.7% of squalene and has d_4^{20} 0.8767; acid number, 0.22; saponification number, 54.0; iodine number, 259.8; n_D^{20} 1.4860; unsaponifiable substances, 71.38% containing, besides squalene, selachyl, and batyl alcohols.

Oil from *Zameus squamulosus* and *Centroscyllium owstonii* contains

42.9% of squalene and has d_4^{25} 0.8816; acid number, 0.88; saponification number, 70.9; iodine number, 225.0; n_D^{20} 1.4825; unsaponifiable substances, 57.17% including squalene, selachyl, and batyl alcohols.

G. W. R.

Autolysis. VIII. The Nature of the Autolytic Enzymes.

H. C. BRADLEY (*J. Biol. Chem.*, 1922, **52**, 467—484).—Dernby (A., 1917, i, 500; 1918, i, 464) has described the autolytic enzymes as closely related to pepsin, trypsin, and erepsin, and has suggested that a mixture of these three enzymes is responsible for the autolysis of tissue. In the present paper, objection is taken to the application of these terms, which connote definite properties, to other proteases, unless these can be shown to have closely similar properties. The presence of erepsin (or the ereptases) in tissue is conceded; evidence, however, is advanced to prove the absence of both pepsin and trypsin. Thus, autolysis of liver or kidney occurs most rapidly in acid mixtures, the optimum P_H being 4.0 to 4.5, and is practically inhibited at P_H 8. Yet in the presence of trypsin the digestion of these organs resembles autolysis of the pancreas and proceeds most favourably at the last-named P_H value. It is evident that trypsin is absent from both liver and kidney. The absence of pepsin is more difficult to prove, since the action of this enzyme, like autolysis, is favoured by acidity. Addition of pepsin, however, to fresh tissue mixture (kidney or liver) at acidities from P_H 6.30 to 1.18 increases autolysis in every case, but the increase is smallest at the optimum for autolysis alone. Moreover, by estimating the amount of primary cleavage by the tyrosine reaction of Folin and Denis (A., 1912, ii, 1012), it is found that, whilst the action of the liver protease is inhibited at P_H 2.6+, that of pepsin not only continues at this acidity but also proceeds most rapidly at P_H 1.2+.

The hypothesis of the autolytic mechanism previously advanced (A., 1916, i, 582) is now extended. At an average P_H of 7.4, the tissue proteins are present as salts of sodium, potassium, and calcium, and in this form are not digested by the autolytic enzymes. With the development of acidity, however, free proteins or acid-protein salts are formed which then undergo cleavage, under the influence of an enzyme which is designated primary protease, into proteoses and peptones. The latter are then rapidly converted into amino-acids by the ereptase present in tissue. The last stage may take place in acid, neutral, or alkaline media, but acidity is essential for the conversion of the native proteins into peptones (cf. Dernby, *loc. cit.*).

E. S.

The Distribution of Quinine Alkaloids in the Animal Organism. EDUARD BOECKER (*Biochem. Z.*, 1922, **130**, 312—320).—Quinine and optochin solutions were injected into guinea-pigs and the quinine and optochin content of the liver and lungs determined approximately by the turbidities produced in aqueous solutions of the extracted alkaloids by potassium mercuric iodide. There is preferential fixation of the alkaloids by the lungs.

H. K.

Cell Penetration by Acids. V. The Estimation of Permeability Changes. W. J. CROZIER (*J. Gen. Physiol.*, 1922, 6, 723—731).—The behaviour was observed of strips of the pigmented mantle tissue of a nudibranch (*Chromodoris zebra*) on immersion in solutions of acids (for the most part dichloroacetic acid). It was found that the rates of penetration by acid and of outward diffusion of pigment bore no relation to one another. Both were facilitated on exposure of the tissue to tension, whereas the rate of acid penetration was accelerated by faradic stimulation and retarded by previous exposure to narcotics such as alcohol and chloroform. C. R. H.

Energy Exchanges in Muscle. OTTO MEYERHOF (*Pflüger's Archiv*, 1921, 191, 128—183; from *Chem. Zentr.*, 1922, i, 153—154; cf. this vol., i, 86, 87).—The "fatigue maximum" with frog muscle in a hydrogen atmosphere or in Ringer's solution corresponds with about 0.35% of lactic acid (calculated on muscle weight). With large additions of carbonate-hydrogen carbonate mixture, the lactic acid is increased to 0.5% and the production of work is also increased. The isometric coefficient, K_m , that is, the tension per centimetre of muscle length per mg. of lactic acid, falls slightly. The "fatigue maximum" is conditioned by the concentration of lactic acid within the muscle. K_m falls during anaerobic stimulation and during narcosis. The ratio of the product of isometric tension and muscle length to work produced decreases with length of stimulus. The "work coefficient," K_a , that is, work produced per mg. of lactic acid, falls with increase of temperature and is smaller under aerobic than under anaerobic conditions. The maximum potential energy developed in one stimulus is probably never more than 75% of the total energy. The relation between chemical and mechanical processes in the muscle of mammals is probably the same as in muscle of cold-blooded animals.

G. W. R.

The Relation between the Endogenous Katabolism and the Non-protein Constituents of the Tissues. H. H. MITCHELL, W. B. NEVENS, and F. E. KENDALL (*J. Biol. Chem.*, 1922, 52, 417—437).—Analyses were made of the tissue of rats maintained both on normal and nitrogen- and sulphur-free diets. The concentration of amino-nitrogen and of total non-protein nitrogen and sulphur was found to be approximately constant, while the value for creatine was slightly higher in the animals on the normal diet. Based on these observations, the view is advanced that the non-protein nitrogenous and sulphur-containing constituents of the tissues serve some special function in the organism other than that of intermediaries in protein metabolism. The endogenous katabolism represents the breaking down, not of tissue protein, but of these substances, which are replaced, normally, from exogenous sources. Only when the latter fail is replacement made by disintegration of body proteins. The conception that protein disintegration is an essential part of cell activity is thus dispensed with.

Creatine, present in the tissues, is an end-product both of endogenous and exogenous metabolism; hence its slightly higher value in the case of the rats on a protein diet. These views are discussed in relation to the literature of the subject.

E. S.

Barium in the Viscera. K. BAUMANN (*Z. Unters. Nahr. Genussm.*, 1922, 43, 383).—A pudding which caused the death of a man through barium poisoning was found to contain 2.34% of barium carbonate. The following quantities of barium sulphate were found in the organs: stomach, liver, and kidneys, 40.0 mg.; urine, 29.0 mg.; intestines, 65.0 mg.; heart, lungs, and spleen, 11.5 mg.; total, 145.5 mg. No barium could be detected in the blood. Three other persons who had eaten of the same pudding suffered from vomiting and diarrhoea, but recovered on the following day.

H. C. R.

Constituents of the Japanese Common Earthworm. II. YOSHIHARU MURAYAMA and SHINJIRO AOYAMA (*J. Pharm. Soc. Japan*, 1922, 482—492; cf. A., 1921, i, 477).—From the hot water extract of the dried earthworm (*Perichaeta communis* sinica, *Lumbricus Spenceri*) the following substances were isolated: xanthine 0.100%, epiguanine 0.163%, adenine 0.078%, guanidine 0.023%, lysine 0.250%, choline 0.004%, alanine 0.031%, valine 0.237%, leucine 0.464%, and phenylalanine 0.025%. Histidine and arginine were not definitely proved to be present.

K. K.

The Presence of Amino-acids in Milk. G. VIALE (*Biochim. terapia sper.*, 1921, 8, 321—324).—Fresh cow's milk which did not contain nitrogen as ammonia had an average content of 8.6 mg. of amino-nitrogen per 100 c.c. The amino-acids of milk (tryptophan, cystine) do not depend on the presence of a tryptic enzyme, but are secreted by the mammary glands.

CHEMICAL ABSTRACTS.

Elimination of Iron in Urine. FRANZ KISCH (*Wiener Arch. inn. Med.*, 1922, 3, 283—296).—The amount of iron eliminated in the urine is not an index of the amount of destruction of the erythrocytes in the body, as the urinary iron may be increased to a marked degree in pathological conditions in which there is either no, or only a slight, increased destruction of erythrocytes, as in chronic nephritis, catarrhal icterus, myeloid leucæmia, and amyloidosis, and, on the other hand, in conditions in which there is a marked increased destruction of erythrocytes as in pernicious anæmia, the urinary excretion of iron may be smaller than in diseases with no increased destruction of erythrocytes. The urinary elimination of iron is markedly increased in all pathological conditions in which a functional injury to the reticuloendothelial system is present or at least probable. The urinary elimination of iron in general shows no change after the intravenous injection of iron. In one case, however, after splenectomy, an intravenous injection of iron was followed by an increased excretion of iron, indicating that the spleen plays a rôle in intermediary iron metabolism.

CHEMICAL ABSTRACTS.

The Presence and Detection of Tyrosine in Urine. O. SCHUMM and A. PAPENDIECK (*Z. physiol. Chem.*, 1922, 121, 1—17).—Tyrosine can be detected by the Frerichs-Städeler method in normal or pathological urines in quantities of 0.2 gram in 400 c.c. of urine, and by Lippich's method in quantities of 0.01—0.02 gram in 100 c.c. of urine. In a number of cases of icterus, no tyrosine was present. Tyrosine was sometimes although not always present in cases of acute yellow atrophy. Sometimes in the absence of tyrosine, crystals resembling tyrosine were obtained. Being, however, easily soluble in water, and giving a blue colour with phosphotungstic acid and sodium carbonate solution, and showing no Millon's reaction, they were identified as disodium urate.

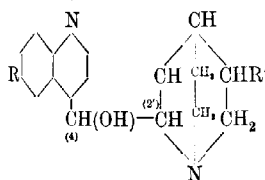
W. O. K.

Hydrogen-ion Concentration of Human Faeces. C. S. ROBINSON (*J. Biol. Chem.*, 1922, 52, 445—466).—The reaction of human faeces is neutral (P_{H} 7.0 to 7.5) in normal subjects, but usually becomes acid under the influence of laxatives. The acidity is apparently regulated in the intestine, variations in the reaction being due to a physiological factor rather than to bacterial action. E. S.

Sensory Stimulation by Alcohols and Chlorohydrins. MARIAN IRWIN (*Amer. J. Physiol.*, 1922, 59, 151—154; 1922, 60, 270—273).—The effect of saturated monohydric alcohols on the sensory mechanism of the worm *Allolobophora foetida*, and their anaesthetic power are in the following order: methyl < ethyl < *tert.*-amyl < *n.*-butyl < *iso*-amyl < *n.*-amyl. Experiments with allyl alcohol, ethylene chlorohydrin, glycerol monochlorohydrin, ethylene glycol, and glycerol show that increase in the number of hydroxyl groups results in a diminution of stimulating efficiency, whilst a great increase in efficiency results when a hydroxyl group is replaced by a chlorine atom, an effect which is independent of hydrogen-ion concentration.

CHEMICAL ABSTRACTS.

[Pharmacological Action of] Cinchona Alkaloids. HUGH W. ACTON (*Lancet*, 1922, 202, 124—128).—The pharmacological action of the cinchona alkaloids is dependent on three factors in the complex alkaloidal molecule (annexed formula): (1) The



grouping of the quinuclidine system around the asymmetric carbon atom at position 2', as shown by their optical rotation. The dextro-rotatory alkaloids (named the "cinchonine series") are more powerful in their effects in toxicity on mice and paramœcium, on inhibiting the action of enzymes, on blood pressure and uterine muscle than the levorotatory alkaloids (named the "cinchonidine series"), which are more powerful in their local anaesthetic effects. (2) The vinyl group (R') in the quinuclidine system. The natural alkaloids are slightly more toxic to paramœcium than the hydroalkaloids. The hydrogenation of the vinyl group to the ethyl group in the hydro-alkaloids renders these alkaloids more difficult

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to oxidise, and they are accordingly not so easily broken down by the body-tissues. They are more toxic to mice, inhibit enzyme action, and cause a greater fall of blood pressure and uterine contraction than the natural alkaloids. (3) The group, R, occupying position 6 in the quinoline ring. The higher members of both series of the hydro-alkaloids are more toxic to mice, paramaecium, bacteria, and leucocytes, and are more powerful as local anaesthetics. This action is not maintained on blood pressure, uterine muscle, and inhibition of enzyme action.

A. A. E.

A New Hypnotic of the Barbituric Acid Series: Ethylbutylbarbituric Acid. PAUL CARNOT and MARC TIFFENEAU (*Compt. rend.*, 1922, **175**, 241—244).—A pharmacodynamical and clinical study was made of a new series of unsymmetrically disubstituted barbituric acids. The hypnotic powers referred to that of diethylbarbituric acid (veronal) as 10, were as follows: methyl-ethylbarbituric acid 5, ethylpropylbarbituric acid 20, ethylbutylbarbituric acid 30, ethylisobutylbarbituric acid 30, ethylisoamylbarbituric acid 30, ethylheptylbarbituric acid 25. As in the symmetrically disubstituted series, the members containing 10 and 11 carbon atoms are the most active, and the ethylbutyl derivative appears particularly suitable for therapeutic use on account of its greater solubility in water, which renders it rapid in action and quickly eliminated. The toxicity of this derivative is proportional to its hypnotic activity, 0.18 gram per kilo. weight of animal being a lethal dose for a mouse, compared with 0.54 gram of veronal. The normal human dose is 0.05—0.1 gram subcutaneously, and 0.1—0.2 gram per os.

G. F. M.

Arsenical Poisoning and the Distribution of Arsenic over the Human Body. H. SCHELLBACH (*Z. Unters. Nahr. Genussm.*, 1922, **43**, 351).—The distribution of arsenic over the body, assuming the weights of the various organs to be normal, in a case of death from arsenical poisoning is calculated as follows: lungs, 6.1 mg.; kidneys, 10.5 mg.; liver, 51.6 mg.; brain, 3.1 mg. expressed as As_2O_3 . The total arsenic taken is estimated as 1 gram of As_2O_3 . The greater part of this was removed from the body again by vomiting and diarrhoea.

H. C. R.

Strychnine. SOMA WEISS and ROBERT A. HATCHER (*J. Pharm. Expt. Ther.*, 1922, **19**, 419—482).—A minimal dose of 0.15 mg. per kilo. body weight of strychnine sulphate produces marked physiological effects on frogs. A method of extraction of strychnine from tissues is described by which, in conjunction with a physiological test on frogs, it is claimed that as little as 0.5 mg. of strychnine in the blood of an adult human being can be detected. Strychnine when added to blood is partly adsorbed by the blood corpuscles (or their stroma after hæmolysis), the proportion adsorbed increasing with increasing concentrations of strychnine.

Strychnine is primarily destroyed by the liver, the kidney only excreting traces which have escaped such destruction.

C. R. H.

Chemistry of Vegetable Physiology and Agriculture.

Increased Velocity and Intensity of Action of Groups of Poisons or Active Drugs on Bacteria and Tadpoles produced by Variation of the Degree of Acidity or Alkalinity. RICHARD LABES (*Biochem. Z.*, 1922, 130, 14—24).—The toxicity of alkaloidal salts to staphylococci and to tadpoles is the more pronounced the greater the alkalinity of the solution, but the toxicity of sodium salts of active acids, for example, benzoic and salicylic, increases with increased acidity, whilst neutral substances, for example, acetanilide and urethane, act independently of the degree of acidity.

H. K.

Formation of Indole, and Indole Reactions. Behaviour of Indole-negative Bacteria. WALTHER FRIEBER (*Zentr. Bakt. Parasitenkunde*, 1921, 87, 254—277; from *Chem. Zentr.*, 1922, i, 420).—In an investigation of the formation or non-formation of indole by bacteria, the principal reactions for indole were examined, using indole, indole derivatives substituted in the 2-position (2-methylindole, indole-2-carboxylic acid), indole derivatives substituted in the 3-position (scatole, *p*-indole aldehyde, indole-3-acetic acid, indole-3-pyruvic acid, indole-3-ethylamine, indole-3-alanine, indole-3-glycylalanine), and indole derivatives substituted in the 2- and 3-positions (indole-2:3-dicarboxylic acid, 2-methylindole-3-alanine, indoxylcarboxylic acid, isatin). The sodium nitroprusside reaction is the most specific, being given only with the free indole nucleus. The Ehrlich reaction (*p*-dimethylaminobenzaldehyde), the vanillin, and the naphthaquinone reactions only require the 3-carbon atom to be free, whilst the Salkowski reaction only requires the 2-carbon atom to be free.

All indole-negative bacteria give the positive Salkowski reaction, probably on account of the formation of indole-acetic acid. The decomposition of tryptophan by indole-positive bacteria is probably accomplished in two stages with indoleacetic acid as an intermediate product. In the presence of easily assimilable carbon compounds, indole-positive bacteria may only perform the first stage of tryptophan decomposition. It is unnecessary to assume an inhibition of proteolysis by carbohydrates. No inhibition of the formation of indoleacetic acid by indole-negative bacteria is shown by carbohydrates. Of the bacteria hitherto described as indole-forming, a large number form indoleacetic acid only.

G. W. R.

Bacteria Fermenting Lactose, and their Significance in Water Analysis. M. LEVINE (*Iowa State Coll. Agric.*, 20, [31], *Bull.* 62).—A critical review of the methods of detection and classification of the colon group of organisms is given. Recent pollution of water is indicated much more certainly by the presence of organisms typified by *Bacillus coli* than by *B. aerogenes* or

Clostridium enteritidis sporogenes. The latter are not considered as characteristic of the intestinal tract and, moreover, persist in water for considerable periods.

A. G. P.

The Beneficial Action of Charcoal Suspensions and other Substances with large Surface Development, such as Colloidal Silica, Ferric Phosphate, and Agar-Agar, on the Formation of Fermentation Gases by *Bacillus coli* in Protein-free Nutrient Media. RICHARD LABES (*Biochem. Z.*, 1922, 130, 1—13).—Finely divided substances of the type named exert a marked beneficial influence in weakly alkaline or acid protein-free nutrient media on the growth of *Bacillus coli* by preventing the detrimental supersaturation of the solution with gaseous products of fermentation.

H. K.

Formation of Phenol by Bacteria. FRITZ SIEKE (*Z. Hyg.*, 1921, 94, 214—223; from *Chem. Zentr.*, 1922, i, 472).—Phenol is formed from the degradation of tyrosine with the removal of the alanine side-chain by bacterial action. Experimental conditions for the culture of phenol-forming bacteria and the morphological, cultural, and serological behaviour of *Bacillus coli phenologenes*, and *B. paracoli phenologenes* are described. Varieties of *B. coli* capable of forming phenol are widely distributed. Indole formation appears to be associated with phenol formation.

G. W. R.

Formation of Bacterial Toxins. II. Diphtheria Toxin. L. E. WALBUM (*Biochem. Z.*, 1922, 130, 25—67).—The optimum temperature for the growth of diphtheria bacilli is 34° and the optimum P_H 7.0. The temperature limits of growth are 20° and 42° and the limits of P_H 5.2 to 8.9. Diphtheria toxin is completely destroyed after six days at 37° if the solution is more acid than P_H 5.5 or more alkaline than P_H 9.3. The optimum P_H for obtaining the toxin is between 7.2 and 7.6. The optimum temperature for toxin formation is 36°. The most suitable medium for preparation of toxin is calf's flesh broth with peptone. The addition of small amounts of manganous chloride has a marked beneficial action on toxin formation in many cases.

H. K.

The Utilisation of Dextrose by the Tubercle Bacillus. C. J. GAMBLE and MARGARET C. HERRICK (*Amer. Rev. Tuberculosis*, 1922, 6, 44—50).—Five strains of *Bacillus tuberculosis*, two human, two bovine, and one avian, consumed dextrose from a liquid medium of 2% dextrose and 0.8% dehydrated broth to the extent of from 12% to 80% (130 to 900 mg.) of the amount originally present (50 c.c.) when estimated by Folin's colorimetric method for blood-sugar (A., 1919, ii, 308; 1920, ii, 337) slightly modified. The amount consumed runs closely parallel to the amount of growth recorded. No differences in the rate of consumption of dextrose by the different strains were detected.

CHEMICAL ABSTRACTS.

Peptase, Lipase, and Invertase of Hæmolytic Streptococcus.

F. A. STEVENS and RANDOLPH WEST (*J. Exptl. Med.*, 1922, **35**, 823—846; cf. *Proc. Soc. Exptl. Biol. Med.*, 1921, **18**, 234).—A method is outlined by which the enzymes of hæmolytic streptococcus can be extracted with comparative ease. The peptolytic enzyme is active between p_{H} 4.4 and 8.7 with an optimum action at p_{H} 7.2. It is destroyed in neutral phosphate solution at a temperature of 57° continued for ten minutes and at p_{H} 5.0 deteriorates slowly at 37°. Concentration experiments with solutions of the enzyme have shown that it resembles other enzymes. It is exceedingly susceptible to chloroform and its action is inhibited by gentian-violet. Casein is attacked, but serum-albumin is not digested after three days at 37°. The invertase is active between approximately p_{H} 5.0 and 8.0 with an optimum at p_{H} 7.0. It is destroyed by a temperature of 52° continued for ten minutes at p_{H} 7.0 or after six hours at 37° at p_{H} 5.0. At this acidity it is more susceptible to heat than the peptase. The lipase is active above p_{H} 5.6. The greatest activity was observed at p_{H} 7.9. It is completely destroyed after heating above 55° for ten minutes and resembles the invertase in its susceptibility to acid.

CHEMICAL ABSTRACTS.

Is the Undecomposed Hydrogen Peroxide or the Oxygen Split from it the Carrier of Disinfecting Action? A. MÜLLER (*Z. Hyg.*, 1921, **93**, 348—371).—Experiments with *Bacillus coli* in the presence of varying amounts of catalase show that the bactericidal action of hydrogen peroxide is a property of the hydrogen peroxide itself, and not of the oxygen liberated from it.

CHEMICAL ABSTRACTS.

Antiseptic Action of Acraldehyde. ALBERT BERTHELOT (*Rev. hyg.*, 1922, **44**, 16—19).—Experiments on *Bacillus coli*, *B. mesentericus vulgatus*, *B. subtilis*, and *Staphylococcus aureus* showed that acraldehyde (stabilised by the addition of 0.2% of catechol) both in aqueous solution and as a vapour, is inferior to formaldehyde in its germicidal and inhibitory powers.

CHEMICAL ABSTRACTS.

The Action of Sublimate, Phenol, and Quinine on Yeast. GEORG JOACHIMOGLU (*Biochem. Z.*, 1922, **130**, 239—248).—From measurements of the loss of weight due to carbon dioxide it is found that the growth of yeast is inhibited by mercuric chloride over the dilutions examined between 1 in 66,000 and 1 in 1,200,000; by quinine hydrochloride at dilutions between 1 in 360 and 1 in 675, but not at higher dilutions; by phenol at 1 in 1000, but not at 1 in 10,000. The so-called Arndt-Schulz law, that small quantities of a poison act in an opposite sense to large quantities, fails.

H. K.

The Occurrence of Emulsin in *Saccharomycetes* and the Existence of a Specific Enzyme Cellobiase. J. GROENEWEGE (*Mededel. Algemeen Proefstation voor den Landbouw*, 1921, No. 9, 1—12).—A new species of yeast, *Williå javanica*, isolated from the

flora developing on moist caoutchouc and capable of splitting amygdalin into glucose, benzaldehyde, and hydrogen cyanide, is described. Pure cultures are easily propagated on usual yeast media; it ferments glucose, lævulose, mannose, sucrose, and raffinose, but not galactose, maltose, lactose, or cellobiose. Culture mediums containing 1% of the glucosides to be investigated were inoculated with the organism and incubated at 33°. After one to two days active splitting was demonstrated in the case of amygdalin, arbutin, æsculin, and salicin by the end-products formed. Fermentation of the glucose liberated occurred in the case of amygdalin and æsculin, but was soon inhibited in the case of the former by the toxicity of the benzaldehyde and hydrogen cyanide formed. By filtering cultures of the organism, drying over calcium chloride, and grinding to a fine powder, a powerful emulsin preparation is obtained which, in respect to purity, activity, and cost, is superior to present commercial preparations. Since *W. javanica* does not ferment cellobiose, the conclusion is that this disaccharide is not hydrolysed by emulsin as its component glucose would be fermented. The power of hydrolysing cellobiose, previously attributed to emulsin, must therefore be ascribed to a specific *cellobiase* occurring as an impurity in ordinary emulsin preparations. It is probable that traces of emulsin reported in brewer's yeast are due to the presence of species of *Willia*.

CHEMICAL ABSTRACTS.

The Fermentation of Glycerol in Presence of Sulphur.

HANS MÜLLER and LEO MÜLLER (*Helv. Chim. Acta*, 1922, 5, 628–629).—In the fermentation of dextrose, the presence of sulphur has the effect of oxidising or dehydrogenating the glycerol, probably according to the equation $C_3H_8O_3 + S \rightarrow C_3H_6O_3 + H_2S$. In presence of sulphur, glycerol is readily attacked by yeast with evolution of carbon dioxide and hydrogen sulphide. The results are of interest in connexion with Neuberg's investigations of fermentation accelerators (*A.*, 1921, i, 81).

E. H. R.

The Chemistry of the Higher Fungi. XV. Chemical Relations between the Higher Fungi and their Substrate.

II. RUDOLF HASENÖHRL and JULIUS ZELLNER (*Monatsh.*, 1922, 43, 21–41; cf. *A.*, 1910, i, 886; 1921, i, 212).—In previous papers (*A.*, 1914, i, 913; 1920, i, 131), the physico-chemical characteristics of heterotrophic phanerogams were to a certain extent elucidated, and an attempt is now made to apply these results to the higher fungi, making use of old and new experimental data. The water content of a fungus is generally higher than that of its substrate or host. The composition of the mineral matter in fleshy fungi is very similar to that in phanerogams, potassium and phosphate being the principal constituents, calcium low, often less than the magnesium, sodium very low, except perhaps in some manure fungi, and iron always present, although sometimes in very small quantities. Precisely what elements are necessary to fungus growth, it is difficult to say; certainly potassium and phosphorus, but calcium is doubtful. The constitution of the substrate appears

not to influence the composition of the ash in fleshy fungi. Data concerning the ash constituents of woody and leathery forms are scanty, and new ash analyses are given of the following: *Polystictus microloma* (Léviér), *Polyporus fomentarius*, L., *P. borealis*, and *Auricularia mesenterica*, Fr. These differ in some respects from the fleshy forms in that potassium is lower and calcium higher. In *Trametes suaveolens*, *Polyporus ignarius*, and *P. fomentarius* calcium sulphate is specially high, and *Polystictus microloma* is extraordinarily rich in sodium chloride. In general, the fungi contain a high proportion of soluble salts, which are necessary to maintain the high osmotic pressure required in the sap of plants containing a high percentage of water. A number of experiments were made to compare the osmotic pressures in different fungi and their hosts, the osmotic pressure being calculated from the analytical figures, assuming the soluble substances present to be dissolved in the total water content. In almost every case, the osmotic pressure of each soluble constituent was higher in the fungus than in the host. In a number of cases, the osmotic pressure was determined from the freezing-point depression of the pressed sap or of an aqueous extract of the fungus reduced to the same concentration as the sap. When the results were compared with isotonic solutions of mannitol and potassium nitrate, it appeared that the mineral constituents found in the ash were far from sufficient to account for the high osmotic pressure of the sap. The discrepancy may be accounted for if a large proportion of the water in the sap, up to 80%, is combined with colloids as water of hydration. It is concluded that the physical and chemical characteristics of the phanerogams are common to the higher fungi.

In connexion with the problem of the manner in which the material of the host is made available for the nourishment of the fungus, experiments were made with the object of detecting cellulose- or lignin-splitting enzymes in a number of fungi, including *Polyporus ignarius*, *P. hirsutus*, *Trametes suaveolens*, *Leuzites sepia*, and *Armillaria mellea*, but without success. Analyses were made of a specimen of oak on which *P. ignarius* had been parasitic. The oak had lost 74% of its weight, as shown by its specific gravity, yet although it had lost the whole of its starch, sugar, and tannin, its composition was otherwise not different from that of healthy oak, showing that the material of the oak was taken up equally by the fungus.

E. H. R.

The Arsenic Content of some of the Marine Algae. A. J. JONES (*Pharm. J.*, 1922, 109, 86—87).—Algae generally appear to contain a certain proportion of arsenic, varying from about 0.01% in the coarser varieties such as *Laminaria* and *Fucus sp.* to as little as 0.0005% in the so-called edible seaweeds such as "Irish moss" (*Chondrus crispus*), the above percentages being calculated on the air-dried weed.

G. F. M.

Influence of Calcium on the Utilisation of the Reserve Material during the Germination of Seeds. L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1922, 175, 249—252).—In order

to determine whether the favourable influence of calcium salts on germination was due to an activation of the hydrolytic enzymes, or of the enzymes concerned in what may be described as the synthetic phase of germination, the juice of the germinating seeds of maize, wheat, radish, etc., was examined refractometrically for their soluble contents. It was found that calcium salts were practically without influence on the dissolubility of the reserve food material. An analysis of the juice of germinating maize, with and without calcium salts, indicated a smaller total amount of dissolved solids in the former case, although the ratio of the amount of sugars present was slightly higher than the ratio of the other constituents, which might indicate a slight activating effect on maltase. The general conclusion is drawn that the favourable influence of calcium salts is specially directed to accelerating the action of the still unknown enzymes concerned in the synthetic phase, that is, the building-up of celluloses, etc., from the soluble food material of the juice. G. F. M.

The Rôle of Manganese in Plants. J. S. McHARGUE (*J. Amer. Chem. Soc.*, 1922, **44**, 1592—1598).—Radish, Alaska garden pea, Canada field pea, cowpeas, lettuce, tomatoes, spinach, carrots, onions, garden beans, cabbage, wheat, oats, clover, and velvet beans, when grown in a medium which did not contain manganese, made a normal growth for six or eight weeks, but thereafter developed a chlorotic condition and failed to make further growth of any consequence. The normal condition of the plants during the first few weeks of growth is accounted for by assuming that the manganese which the seed contained was sufficient to maintain a normal metabolic process during this part of the plant's growth, and that the chlorotic condition was a result of the lack of a further supply of available manganese. The first effect to be noted in the growth of plants from which manganese has been withheld is a lack in the development of chlorophyll in the newly formed tissues or the growing parts of the plant. This condition increases with time and finally results in the tips of the branches dying back and a cessation of further growth of any consequence in the plant. Leguminous plants appear to be more sensitive than non-legumes to lack of manganese, thus suggesting that manganese is concerned in nitrogen assimilation and the synthesis of proteins.

Apparently manganese plays the rôle of a necessary catalyst in plant metabolism, and together with iron functions in the synthesis of chlorophyll. H. W.

The Relative Distribution of Carbohydrates in Foliage in its Dependence on Water Content. H. SCHROEDER and TRUDE HORN (*Biochem. Z.*, 1922, **130**, 165—198).—If detached leaves of plants be allowed to wither the starch content falls off much more rapidly than if the leaves be kept turgid by water. In the case of detached leaves of *Tropaeolum majus* kept in the dark, if starch be present the sucrose content increases with diminution of the water content and decreases as the water content increases.

The sucrose content is independent of the content of hexoses if these be expressed in the form lævulose+dextrose. It is probable that the same happens in undetached leaves of plants. H. K.

Antagonistic Ion Effects. WIDAR BRENNER (*Hyllningskrift tillägnad Ossian Aschan*, 1920, 36—44).—Experiments were carried out on cabbage leaves to show that the coagulation of a negative, hydrophilic colloid by hydrogen-ions is counteracted by certain neutral salts. The kations investigated, in the presence of chlorine anion, have a counteracting influence in the following order: $\text{Ca} > \text{Mg} > \text{K} > \text{Na}$. In connexion with nitrate ions the calcium-ion effect is greatly diminished and magnesium and potassium ions produce no effect. CHEMICAL ABSTRACTS.

Effect of different Kinds of Solar Radiation on the Formation of Essential Oils in Plants. E. CANALS (*Bull. Sci. Ind. Roure-Bertrand fils*, 1921, [iv], 3, 8—13; from *Chem. Zentr.*, 1922, i, 580—581).—Plants of *Thymus vulgaris* were grown under glass of different colours. Plants receiving white and blue light were little different from open-air plants. With red light, however, growth was altered and flowering inhibited. The essential oil from plants under red light contained 25.5% of thymol, from plants under blue light 36% of thymol, and under white light, 45% of thymol. The oil from open-air plants contained 52.5% of thymol. The thymol content of the oil decreases with the decrease in the xerophilous character of the plants. G. W. R.

Capsella bursa pastoris, Moench. R. WASICKY (*Ber. deut. Pharm. Ges.*, 1922, 32, 142—153).—In order to determine whether *Capsella bursa pastoris* can serve as an ergot substitute, capsella plants in all stages of development were collected in both an infected and a fungus-free condition. The plants were extracted both with water and with alcohol of various concentrations, and fluid extracts were thus prepared from the whole plants and also after separation into their individual organs, such as leaves, stems, fruits, etc. Care was taken to avoid as far as possible any disturbing factors, such as high temperatures, infection, etc. The extracts were injected intravenously into rats, guinea pigs, and rabbits, and also into isolated frog's hearts and the intestines of rats, etc. It was shown that the action of the drug when free from fungus was only such as must be attributed to the potassium salts they contained. The fruits alone contained in addition choline or similar bases, but only in such quantity as to have a negligible influence on the therapeutic action. Infected plants had a more pronounced action probably on account of the presence of proteinogenous bases similar to those in ergot, but in any case the activity fell far below that of an ergot extract. Attempts to isolate acetylcholine according to the directions given by Boruttau and Cappenberg (A., 1921, i, 487) led to a negative result. It is maintained that the platonic chloride method of evaluating capsella extracts (*loc. cit.*) and Grunne's modification (A., 1921, ii, 720) are valueless, as the precipitates do not consist of choline compounds at all, but are potassium salts. Clinical

experiments confirm the uselessness of capsella preparations for staunching uterine bleeding, and it is concluded that the drug is quite useless as an ergot substitute.

G. F. M.

Copal Oil, a New Fat of the Belgian Congo. J. PIERAERTS (*Mat. grasses*, 1922, **14**, 6094—6097).—The most important source of copal oil is from the fruit of the *Copaifera Demeusei*. The constants of the oil are: d_{20}^{25} 0.9165; n_D^{20} 1.4601; saponification number, 196.2; iodine number, 59.5; Reichert-Meissl number, 0.67; Polenske number, 0.30; Hehner number, 94.6. A drying test made with the oil for one hundred and twenty days resulted in the major portion of the oil retaining its original consistency. The change in weight did not exceed 0.01%. The constants of the fatty acids are: solidifying point, 42°; n_D^{25} 1.4488; neutralisation number, 196.1; mean molecular weight, 286; iodine number, 62.9; solid acids, 55%, liquid acids, 45%. The constants of the solid acids are: solidifying point, 58.5 to 60°; iodine number, 40.2; neutralisation number, 153.9; saponification number, 171.2. The iodine number of the liquid fatty acids was 138.9.

CHEMICAL ABSTRACTS.

The Oils of Grape Seeds. The Solid Fatty Acids. Method of Separation of Stearic and Palmitic Acids. ÉMILE ANDRÉ (*Compt. rend.*, 1922, **175**, 107—109).—From the solid fatty acids obtained from the oil of grape seeds the author has isolated stearic, palmitic and melissic acids. The last-named acid probably comes from the waxy layer on the outer covering of the seeds. Palmitic and stearic acids may readily be separated for identification by fractional precipitation of their lithium salts from solution of the mixed acids in 95% alcohol.

W. G.

Purging Nut Tree Oil. L. (*Mat. grasses*, 1922, **14**, 6099—6101).—The tree, *Jatropha curcas*, Linn., is related to the castor and croton oil plants. The dry seeds contain from 34 to 37% of oil. The constants of three samples of oil from different localities varied as follows: d_{20}^{25} 0.9183 to 0.9207; saponification number, 191 to 193; iodine number, 95.6 to 104.3; acetyl number, 18.7 to 25.4; Reichert-Meissl number, 0.37 to 0.60; Polenske number, 0.22 to 0.24. Heating at 100° for twenty-two hours discolours the oil, and exposing to light and air for seven hours produces a slight drying. The cake contains purgative substances.

CHEMICAL ABSTRACTS.

Nitrogenous Metabolism of the Higher Plants. II. The Distribution of Nitrogen in the Leaves of the Runner Bean. ALBERT CHARLES CHIBNALL. (*Biochem. J.*, 1922, **16**, 344—362; cf. A., 1921, i, 482).—Extensive estimations have been made of the nitrogen content of the leaves of the runner bean, particularly to determine seasonal and diurnal variations and the results of starvation. The results indicate the synthesis of protein from nitric-nitrogen through monoamino-nitrogen, and then the degradation of protein to "other-nitrogen" followed by translocation from the leaf.

W. O. K.

Organic Chemistry.

The Energy of the Atomic Linkings in Saturated and Unsaturated Hydrocarbons. J. P. WIBAUT (*Rec. trav. chim.*, 1922, **41**, 441—460).—A theoretical discussion in which it is pointed out that the energy of an ethylenic bond is, from thermochemical data, approximately 20 Cal. less than double the energy of the single bond. A similar relation may be deduced for aromatic hydrocarbons, and also for partly reduced substances derived from them, although in this class of compounds the difference between the energy of the two linkings is estimated at from 7 to 12 Cal. These deductions include accumulated errors, but are derived from a study of all the available data. From the work of Fajans (A., 1920, ii, 354), it appears that the value of a single carbon linking is at least 70 Cal., therefore the smallest value for a double bond is about 120 Cal. and for a triple bond about 160 Cal. By the combination of two CH_2 groups to form C_2H_4 , considerably more energy is evolved than by the combination of two CH_3 groups to form C_2H_6 . No value of the carbon-hydrogen linking is taken into account in the above inferences, so that the conclusions are drawn from the smallest value that can be assigned to a single carbon linking. It results from a consideration of the fact that the thermochemical data do not accord with the usual stereochemical view of the ethylenic bond, and its representation by means of a state of strain existing between the two carbon atoms thus bound.

H. J. E.

Preparation of Propylene in a Pure Condition. MAX TRAUTZ and KARL WINKLER (*J. pr. Chem.*, 1922, [ii], **104**, 44—52).—Propylene is prepared in very good yield by passing propyl, or, better, isopropyl alcohol over aluminium oxide or "graphitiegelmasse" (Ipatiev, A., 1902, i, 335) at 360° , preferably under diminished pressure. It is purified by passing through a receiver cooled in ice, then over calcium chloride and potassium hydroxide, through a vessel cooled in a mixture of toluene and solid carbon dioxide, and finally over calcium chloride. Pure propylene has the following constants: vapour density, 0.2% higher than corresponds with the molecular weight: d_4^{20} , 0.647; b. p. $-47.8^\circ/750$ mm.; it does not solidify in liquid air; n_{D}^{20} yellow 1.00102. The specific volume of a mixture of cyclopropane and propylene in the liquid condition is additive, and thus the measurement of the specific volume of such a mixture gives the proportion of the constituents.

W. O. K.

γ -Methyl- Δ^7 -pentene. HORTENSE VAN RISSEGHEM (*Bull. Soc. chim. Belg.*, 1922, **31**, 213—222).—Dehydration of methyl-diethyl-carbinol by means of *p*-toluenesulphonic acid yields a mixture of

VOL. CXXII. i.

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the two stereoisomeric γ -methyl- Δ^2 -pentenes which may be separated by fractional distillation. The following physical constants were determined: for the fraction b. p. 65.1—65.7°, d_4^{20} , 0.7220; $n_{\text{H}_2\text{O}}^{15}$, 1.3974; $n_{\text{H}_2\text{O}}^{15}$, 1.4058; $n_{\text{H}_2\text{O}}^{15}$, 1.4108; $n_{\text{H}_2\text{O}}^{15}$, 1.3997; for fraction b. p. 69.9—70.2°, d_4^{20} , 0.7022; $n_{\text{H}_2\text{O}}^{15}$, 1.4047; $n_{\text{H}_2\text{O}}^{15}$, 1.4136; $n_{\text{H}_2\text{O}}^{15}$, 1.4186; $n_{\text{H}_2\text{O}}^{15}$, 1.4072. It is claimed that this is the first separation of isomeric ethylenic hydrocarbons that has been effected. Both substances are transformed into methyl ethyl ketone on oxidation with chromic acid. The action of bromine on each is merely additive, but aqueous hydrochloric acid acts on the fraction of lower boiling point as an isomerising agent. Like other ethylenic substances, these hexenes undergo spontaneous oxidation with formation primarily of peroxides and subsequently of aldehydic substances.

H. J. E.

The Explosion of Acetylene and Nitrogen. II. WILLIAM EDWARD GARNER and KICHIMATSU MATSUNO (T., 1922, 421, 1729—1736).

The Chlorination of *n*-Butyl Alcohol. H. GAULT and R. GUILLEMET (*Compt. rend.*, 1922, 175, 367—369).—An experimental study carried out under various conditions, in presence of metallic iron together with control experiments in absence of the catalyst, shows that the proportion of alcohol unattacked by chlorine is greater in the absence of iron. Chlorination of the heated alcohol yields a smaller proportion of products of high boiling point; this is due to the fact that increase of temperature tends to the formation of acetals and thus at the higher temperature the fixation of chlorine is less complete. The mechanism of the reaction seems to depend in the first place on the oxidation of the alcohol; this is followed by the conversion of the aldehyde into an acetal by the hydrochloric acid which is formed simultaneously. Four substances are produced in quantity, one of which, b. p. 138—140°/15 mm., has been studied. It appears to be a dibutyl acetal of a dichlorobutyraldehyde and forms 60—70% of the total yield. Little effect is produced on it by hydrolytic agents; concentrated sulphuric acid decomposes it almost quantitatively into *n*-butyl alcohol. Oxidation by chromic acid in acetic acid solution yields butyl acetate or, in dilute aqueous solution, butyl butyrate, and in both cases a butyl dichlorobutyrate of b. p. 110°/15 mm. Acetic anhydride yields butyl acetate. The authors conclude that the two atoms of chlorine that are fixed form part of the aldehyde chain, and they assign to the compound the formula $\text{C}_4\text{H}_6\text{Cl}_2(\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3)_2$.

H. J. E.

Derivatives of Trihalogen *tert*-Butyl Alcohols. IV. **The Benzoyl Ester of Tribromo-*tert*-butyl Alcohol or Bromotone Benzoyl Ester.** T. B. ALDRICH and JULIA E. BLANNER (*J. Amer. Chem. Soc.*, 1922, 44, 1759—1762; cf. A., 1916, i, 115; 1917, i, 77; 1919, i, 62; 1920, i, 611).—*Bromotone benzoate* [tribromo-*tert*-butyl benzoate], monoclinic crystals, m. p. 90°, is prepared in excellent yield when molecular proportions of benzoyl

chloride and tribromo-*tert*.-butyl alcohol are heated together on a water-bath until hydrogen chloride ceases to be evolved. It is not readily saponified. In striking contrast to brometone, the halogen atoms are not readily removed by treatment with sodium hydroxide solution. Its insolubility probably accounts for its lack of physiological action. The interaction of the trihalogeno-*tert*.-butyl alcohols with the three nitrobenzoyl chlorides leads to the formation of the corresponding nitrobenzoates; the meta-compounds are also obtained by treatment of the parent esters with concentrated nitric acid. The following substances are described: *Trichloro-tert*.-butyl *o*-nitrobenzoate, monoclinic plates, m. p. 91°; *m*-nitrobenzoate, monoclinic plates, m. p. 87°; *p*-nitrobenzoate, flat needles, m. p. 145°; *tribromo-tert*.-butyl *o*-nitrobenzoate, monoclinic plates, m. p. 97°; *m*-nitrobenzoate, flat needles, m. p. 121°; *p*-nitrobenzoate, needles, m. p. 148°. The esters are not as active physiologically as the alcohols from which they are derived, possibly owing to their insolubility in water.

H. W.

The Oxidation of Acetylcarbinol with Potassium Permanganate. WILLIAM LLOYD EVANS and ORA L. HOOVER (*J. Amer. Chem. Soc.*, 1922, **44**, 1730—1741; cf. A., 1916, i, 362; 1919, i, 514, 572).—The series of experiments described in this communication is designed to elucidate the following points: (1) the influence of the initial concentration of the alkali on the character and amounts of the products of the reaction; (2) the effect of variation of temperature on the nature and quantities of the products; (3) the mechanism of the change in neutral and alkaline solution.

Four general reactions, represented by the equations $[\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{OH} \rightleftharpoons \text{CH}_3\text{CHO} + \text{CH}\cdot\text{OH}; \text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{OH} \rightleftharpoons \text{CH}_3\text{CO}\cdot\text{CH}\cdot + \text{H}\cdot\text{OH}; \text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{OH} \rightleftharpoons \text{CH}_3\text{C}(\text{OH})\cdot\text{CH}\cdot\text{OH}; \text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{OH} \rightleftharpoons \text{CH}_3\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}]$, are involved in the oxidation of acetylcarbinol in neutral or alkaline potassium permanganate solutions. The extent to which each reaction contributes to the general oxidation of acetylcarbinol depends on the initial concentration of the alkali used.

Carbon dioxide and acetic acid are the sole products of the oxidation with neutral permanganate solutions at 25°, 50°, 75°, and 100°. Oxalic acid is found in all alkaline solutions except those in which the concentrations of the base are exceedingly small.

The production of carbon dioxide at 50°, 75°, and 100° is in excess of that which corresponds with one gram atom equivalent of carbon. Acetylcarbinol is oxidised to give this excess of carbon dioxide through the following steps: pyruvaldehyde, (hydroxypyruvaldehyde), pyruvic acid, hydroxypyruvic acid, formylglyoxylic acid, and glyoxylic acid. The concentration of the alkali at the peaks of the carbon dioxide yields is approximately the same as that corresponding with the minimum yields for oxalic acid; the yield of carbon dioxide decreases as that of oxalic acid increases.

The general effect of the alkali is to increase the velocity of the oxidation, to convert pyruvaldehyde into lactic acid, to increase

the enolisation of pyruvic acid, to increase the enolisation of the acetylcarbinol according to the schemes: $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH} \rightleftharpoons \text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{OH}$ and $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH} \rightleftharpoons \text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, and to lower the dissociation point of acetylcarbinol in accordance with the expression: $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OK} \rightarrow \text{CH}_2\cdot\text{CO}\cdot\text{CH}\cdot + \text{KOH}$.

The yields of acetic acid reach a second maximum and those of oxalic acid a second minimum in solutions in which the initial concentration of potassium hydroxide is approximately 0.5*N*; these points are also a function of the temperature.

The effect of temperature on the yield of the products of oxidation varies in different regions of alkalinity. H. W.

Action of Bromine on Methylal. FRANZ FEIST (*Z. anorg. Chem.*, 1922, **35**, 489—490).—The addition of bromine to methylal, cooled in a freezing mixture of ice and salt, leads to the formation of methyl bromide, *dibromomethylal*, $\text{CBr}_2(\text{OMe})_2$, and products of higher boiling point which could not be freed from an excess of bromine without undergoing decomposition, and have not been investigated further. *Dibromomethylal* is a colourless liquid with a somewhat unpleasant odour, b. p. 14.5—15°. It is very readily hydrolysed. It is highly reactive and, at 0°, effects the methylation of a series of substances which are not affected by methyl bromide under similar conditions. When treated with water, it gives methyl alcohol, hydrogen bromide, and carbon dioxide, together with formaldehyde and formic acid. With aniline dissolved in ether, it yields methylaniline hydrobromide and carbon dioxide. It converts β -naphthol into β -naphthyl methyl ether, ethyl sodium-malonate in the presence of light petroleum into ethyl methyl-malonate, and ethyl sodiumacetate into ethyl methylacetate. Cinnamic acid is not esterified by *dibromomethylal*, whereas its sodium salt is converted into methyl cinnamate. H. W.

Vapour Densities at Low Pressures and over an Extended Temperature Range. I. Properties of Ethylene Oxide compared to Oxygen Compounds of Similar Molecular Weight. O. MAASS and E. H. BOOMER (*J. Amer. Chem. Soc.*, 1922, **44**, 1709—1728).—The vapour pressure, boiling point, melting point, surface tension, critical temperature, viscosity, and liquid density of pure ethylene oxide have been determined, and these physical constants compared with those of methyl ether, ethyl alcohol, and acetaldehyde. The following data are recorded: m. p. -111.3°, b. p. 10.73°, critical temperature, 192.0°, molecular heat of vaporisation, 6.00 Cal.; *K* (Ramsay and Shields), 1.79; surface tension at the boiling point, 25.8; total surface energy, 73.1; molecular volume at the boiling point, 49.9; molecular viscosity at slope 0.0000323, 0.0412; molecular viscosity at slope 0.0000987, 0.0785. The particularly good agreement of the surface tension data over the range -52.0° to +20.0° with the modern theory is pointed out. The comparison of the physical properties with those of the other substances mentioned emphasises the ring structure of ethylene oxide. The investigation of the oxonium compound formation, by means of freezing-point curves of the

binary systems between ethylene oxide and chlorine, bromine, water, hydrogen chloride, and hydrogen bromide, respectively, furnishes evidence of the existence of double compounds, $C_2H_4O.Cl$, $C_2H_4O.Cl_2$, $C_2H_4O.Br$, $C_2H_4O.Br_2$, $C_2H_4O.6H_2O$, and the probable existence of a compound with hydrogen bromide. The compounds with chlorine and bromine exist only at low temperatures, at higher temperatures an interatomic rearrangement taking place. The vapour density of ethylene oxide over the temperature range $14-100^\circ$, and the pressure range 0-1 atmosphere was measured, and it is pointed out that these data will serve for obtaining data on the relative molecular attraction.

J. F. S.

Preparation of Water-soluble Derivatives of Aryl Ethers of Higher Aliphatic Alcohols. ELEKTROCHEMISCHE WERKE

(L. M. B. H., HEINRICH BOSSHART, and DAVID STRAUSS (D.R.-P. 344878; from *Chem. Zentr.*, 1922, ii, 834-835).—Aryl alkyl ethers, obtained by condensation of naphthols or phenols with halogen-substituted aliphatic hydrocarbons containing at least sixteen carbon atoms, using appropriate catalysts, are sulphonated until they are soluble in water. *Monochloroparaffin*, obtained by chlorination of paraffin, is a white, wax-like substance having m. p. $35-46^\circ$; it gives, on heating with phenol, potassium carbonate, and carbon in a reflux apparatus, *phenoxyparaffin*, a soap-like mass having m. p. 60° . The corresponding *sulphonic acid* is a semi-solid, fat-like substance soluble in water. Its dilute aqueous solution may be used for tanning. Similar sulphonic acids may be obtained from *o*- or *p*-tolylloxyparaffin and cetylguaiacol. *Phenoxychloroparaffin*, obtained from *dichloroparaffin* (m. p. $40-60^\circ$) and phenol, and *z*- or *β*-*naphthoxyparaffin* are similar to phenoxy-paraffin.

G. W. R.

The Reactivity of Alkyl Iodides with Sodium Benzyloxide and the Effect of Temperature on such Reactions. PERCY CHARLES HAYWOOD (T., 1922, 421, 1904-1921).

Action of Silver Sulphate in Sulphuric Acid Solution on certain Halogen Derivatives. E. A. SCHEROV (*Bull. Inst. Polyt. Irano-Voznesensk.*, 1921, 4, 169-170).—A solution of silver sulphate in concentrated sulphuric acid acts on methyl iodide, ethyl chloride or bromide, or ethylene bromide more energetically than an alcoholic solution of silver nitrate of identical concentration. The reaction proceeds in 100% sulphuric acid, but is greatly influenced by the presence of water, the function of which has not yet been explained.

With ethyl bromide and a strong sulphuric acid solution of silver sulphate, the products obtained include silver bromide and ethylsulphuric acid, but not ethyl sulphate: the latter undergoes only slow conversion into ethylsulphuric acid under the influence of concentrated sulphuric acid and is hence not formed even as an intermediate product. The amount of ethylsulphuric acid separable as barium salt amounts to only about 77% of the calculated quantity. Since in the sulphuric acid solution the silver

probably exists as the complex ion AgSO_4' , the energetic action on alkyl haloids is scarcely compatible with Bruyn and Steger's theory (A., 1899, i, 745, 849), which assumes electrolytic dissociation of the silver salt and alkyl haloid.

T. H. P.

The Autoxidation of Organic Sulphur Compounds. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1922, [iv], 31, 762—789; cf. this vol., i, 261).—A general survey of the subject in which the bearing of the work of Mourcu and Dufraisse (this vol., i, 250) on organic sulphur compounds is discussed. The facts observed in studying the effect of pressure on oxidation of phosphorus (Jorissen, A., 1921, ii, 79, 688) are considered in their relation to the oxidation of sulphur compounds. As a provisional hypothesis, the author suggests that sulphur compounds form a group intermediate between those substances which are spontaneously inflammable in air or oxygen and others, such as benzaldehyde, which undergo oxidation with the formation of more stable compounds. H. J. E.

Behaviour of $\beta\beta$ -Dichlorodiethyl Sulphide. S. P. KRAMER (*Kolloid Z.*, 1922, 31, 150—151).—When $\beta\beta$ -dichlorodiethyl sulphide is shaken with 5 c.c. of 1% sodium silicate solution, it is shown that in two hours each drop of the sulphide is surrounded by a sheath of colloidal silicic acid, and in forty-eight hours the whole tube is filled with colloidal silicic acid gel. The dichlorodiethyl sulphide is hydrolysed to dihydroxydiethyl sulphide, and the hydrochloric acid set free liberates colloidal silicic acid. By this change, the oil has lost its inflammatory properties and may be placed on the skin with impunity. A 10% solution of $\beta\beta$ -dichlorodiethyl sulphide in olive oil or cod-liver oil, when added to 1% sodium silicate solution, is immediately emulsified and on centrifuging the hydrolysed product separates. The above experiments furnish a method of treatment of burns produced by "mustard gas." The wound is washed and covered with olive oil or cod-liver oil and then washed with a 1% solution of sodium silicate. It is then covered with a compress moistened with 3% sodium silicate solution so long as it remains inflamed.

J. F. S.

Improvements in the Process of Converting Organic Acids into Esters. ERNST ZOLLINGER-JENNY (Brit. Pat. 183897).—The conversion of organic acids, other than polyhydroxy-fatty acids, into esters is greatly simplified and accelerated by the use of zinc or tin or other metals of the periodic group including tin. The metal need not necessarily be in a finely-divided state; it may be introduced into the apparatus in the form of a regulus, or be applied to the floor or wall or to a body inserted into the vessel. As soon as the temperature of reaction is reached and maintained, the conversion sets in and proceeds with considerable speed until the mixture is neutral. It is not essential to have an excess of the alcoholic component; the mixture may be in stoichiometrical proportions. Organic acids of the highest molecular weights, including resin acids, can be converted into esters in this way, and the process can be applied, not only to pure, free fatty acids,

but also to fatty acids mixed with fat or diluted with primary monohydric or other alcohols. H. W.

The Solubilities of the Alkali Formates and Acetates in Water. NEVIL VINCENT SIDGWICK and JOSEPH ALFRED HECTOR ROBERTS GENTLE (T., 1922, **121**, 1837—1843).

The Transformation of Sodium Formate into Oxalate. C. MATIGNON and [Mlle] G. MARCHAL (*Bull. Soc. chim.*, 1922, [iv], **31**, 789—796; cf. Merz and Weith, A., 1882, 1049).—A study of the reactions which take place on heating sodium formate to 440° shows that its decomposition is rapid. No appreciable difference is made in the yield of sodium oxalate by heating in a vacuum when compared with the results obtained by heating in air in presence of a catalyst. Sodium hydroxide when present to the extent of 4% is a satisfactory catalyst and increases the yield of oxalate from 50% to 85%; as it is normally present as impurity in commercial sodium formate, a better yield is obtained from the latter than from the pure substance. A method of isolating the oxalate from the reaction mixture is described. H. J. E.

Preparation of Acetic Anhydride, Acetaldehyde, or Acetic Acid from Ethylidene Diacetate. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (D.R.-P. 346236; from *Chem. Zentr.*, 1922, ii, 808).—Ethylidene diacetate is heated under reduced pressure in the presence of contact substances. The acetic anhydride thus formed is separated by distillation from paracetaldehyde with or without depolymerisation or oxidation of the latter. For example, after heating ethylidene diacetate (400 parts) with sulphuric acid (8 parts) at 70—80° under 100 mm. pressure, the resultant mixture of acetic anhydride and paracetaldehyde is either maintained at a medium temperature or heated with a depolymerising substance, whereby acetaldehyde is obtained and separated by distillation. Alternatively, the paracetaldehyde is oxidised to acetic acid by a stream of oxygen. G. W. R.

Acetic Acid Esters of Multivalent Alcohols. I. Is there a Connexion between the Velocity of Saponification and the Method of Preparation of the Glycerol Acetins? L. SMITH (*Z. physikal. Chem.*, 1922, **102**, 54—73).—After a short discussion on the constitution of the glycerides, the author draws the conclusion that all methods of determining the constitution of these substances which depend on the products of reaction with other substances and the subsequent examination of the products are worthless, and that for the determination of constitution some physico-chemical property must be employed which will allow the glyceride being studied "in statu." Of such physico-chemical properties, the velocity of saponification appears to be most suitable. The author has synthesised mono-, di-, and tri-acetin by a number of methods, and has used the various products to determine the velocity of saponification at 25°. The results show that the velocity of the acetins in alkaline aqueous solution is within

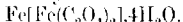
the limits of experimental error (1%), independent of the method of preparation.

J. F. S.

Decomposition of Methyl Oxalate by Acetic Acid. E. E. TURNER and F. H. H. WILSON (*Proc. Roy. Soc. New South Wales*, 1921, 55, 63—64).—When methyl oxalate is heated with acetic acid in a reflux apparatus, it is more or less completely converted into methyl acetate and oxalic acid. Using acetic acid of 70% concentration, an 83% yield of methyl acetate is obtained; stronger and weaker acids give lower yields. Since methyl oxalate can be readily obtained in a pure state from commercial methyl alcohol, a convenient means is afforded for preparing pure methyl acetate.

E. H. R.

The Preparation of certain Ferrioxalates. G. J. BURROWS and E. E. TURNER (*Proc. Roy. Soc. New South Wales*, 1921, 55, 263—265).—Barium ferrioxalate is obtained by heating in aqueous solution the calculated quantities of ferric sulphate, barium hydroxide, and oxalic acid, and extracting the barium ferrioxalate with boiling water. The salt crystallises in slender, pale green needles of the composition $\text{Ba}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]_2 \cdot 12\text{H}_2\text{O}$. Hydrates containing 7, 21, and 22 molecules of water have been described by various authors. Starting with ferric ammonium sulphate, a barium ammonium ferrioxalate was obtained in addition to the normal barium salt. It crystallises, by spontaneous evaporation of the filtrate from the barium salt, in bright green prisms of the composition $\text{NH}_4 \cdot \text{Ba}[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$. The yellow colour of ferrous oxalate, both in the solid state and in dilute sulphuric acid solution, suggests that it may be in reality ferrous ferro-oxalate,



Cinchonine ferrioxalate crystallises from dilute alcohol in pale green needles having the composition $(\text{C}_{19}\text{H}_{23}\text{ON}_2)_3 \cdot \text{H}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 6\text{H}_2\text{O}$. *Strychnine ferrioxalate*, $(\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2)_3 \cdot \text{H}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 12\text{H}_2\text{O}$, forms pale green leaflets. Attempts to resolve ferrioxalic acid into its optically active components by recrystallisation of the strychnine salt were unsuccessful.

E. H. R.

The Formation and Stability of Spiro-compounds. IX. The Influence on Stability of Groups of High Molecular Weight. STANLEY FRANCIS BIRCH and JOCELYN FIELD THORPE (*T.*, 1922, 121, 1821—1837).

A Method for the Preparation of $\alpha\beta$ -Trialkylated Glutaric Acids. GEORGE ARNAND ROBERT KON and JOCELYN FIELD THORPE (*T.*, 1922, 121, 1795—1803).

Ring-chain Tautomerism. III. The Occurrence of Tautomerism of the Three-carbon (Glutaconic) Type between a Homocyclic Compound and its Unsaturated Open-chain Isomeride. CHRISTOPHER KELK INGOLD, EDWARD ARTHUR PERREN, and JOCELYN FIELD THORPE (*T.*, 1922, 121, 1765—1789).

Zirconyl Citrate. F. P. VENABLE and R. A. LINEBERRY (*J. Amer. Chem. Soc.*, 1922, **44**, 1708—1709).—The addition of ammonium or potassium citrate to solutions of zirconyl chloride gives precipitates, soluble in excess of ammonium citrate, which may be washed free from ammonium and potassium compounds. The precipitates are therefore not double citrates, as was stated by Harris (A., 1899, i, 262). Normal zirconyl citrate, $(\text{ZrO})_3(\text{C}_6\text{H}_5\text{O}_7)_2$, may be prepared by the slow addition of a 0.1*M*-solution of citric acid to a freshly prepared 0.1*M*-solution of zirconyl chloride. If the zirconyl chloride is boiled before precipitation, the basic compound, $3\text{ZrO}(\text{OH})_2(\text{ZrO})_3(\text{C}_6\text{H}_5\text{O}_7)_2$, is obtained. J. F. S.

Clupanodonic Acid. M. TSUJINOTO (*Chem. Umschau*, 1922, **29**, 261—262).—The highly unsaturated acid to which the peculiar odour of fish oils is probably due has the formula $\text{C}_{22}\text{H}_{34}\text{O}_2$, and not $\text{C}_{18}\text{H}_{28}\text{O}_2$, although a small quantity of an acid having the latter formula occurs in Japanese sardine oil. Majima and Okada found that the acids obtained by the debromination of the ether-insoluble bromides from Japanese sardine oil gave mainly behenic acid on hydrogenation. Clupanodonic acid has been obtained almost pure by fractionating the methyl esters obtained from the highly unsaturated acids from Japanese sardine oil by the lithium-salt-acetone method. It is a pale yellow liquid not solidifying at -50° , and thick, like vaseline, at -78° . It has a fishy odour and the following characters: d_4^{25} , 0.9398; neutralisation value, 172.5; iodine value (Wijs), 390 (theoretically 384.3); n_D^{25} , 1.5040. The methyl ester has d_4^{25} , 0.9247; b. p. $222^\circ/5$ mm.; n_D^{25} , 1.4960. Clupanodonic acid is one of the most widely distributed compounds in nature, occurring in the oils of all fresh- and salt-water fish, reptiles, and amphibious animals. H. C. R.

The Oxidation of Hydrocarbons, with Special Reference to the Production of Formaldehyde. E. W. BLAIR and T. SHERLOCK WHEELER (*J. Soc. Chem. Ind.*, 1922, **41**, 303—310r).—The limited oxidation of ethylene by oxygen at high temperatures in presence and absence of a catalyst was studied with the object of discovering the most favourable conditions for the production and possible manufacture of formaldehyde. The conclusions of Willstätter and Bommer (A., 1921, i, 93) were confirmed, and to some extent amplified. When a catalyst (platinum gauze) was used, even when the temperature was so low and the time of contact so short that a reaction was barely perceptible, hydrogen and carbon monoxide were the main products. Traces of formaldehyde were detected, however, showing that the course of the oxidation is the same as in absence of a catalyst. Extending Willstätter's and Bommer's experiments without a catalyst, it was found that as the time of heating at any given temperature decreased, the ratio of acetaldehyde to formaldehyde increased: the percentage yield of aldehyde on ethylene increased, and at 540° , heating for 1.5 secs., no carbon monoxide was formed. Decreasing the proportion of ethylene in the mixed gases below the 20% used by Willstätter also increased the yield* of formaldehyde. A number

*kk**

of experiments were made in which the reacting gases were continuously circulated, and a yield of 75% theory of formaldehyde on the ethylene consumed was obtained at 575° with a heating time of 1 second, starting with a mixture containing 19.4% of ethylene and 15.8% of oxygen. It was not found possible to work with mixtures containing less than 14% of ethylene. These are inflammable, the ignition temperature being 546°. Below this temperature the reaction is very slow and the proportion of acetaldehyde formed increases. Ammonia was found to stabilise the formaldehyde as formed, by combining with it to form hexamethylenetetramine; using ammonia in the mixed gases, it was possible to isolate some formaldehyde in experiments in which a catalyst was used. Steam also had a stabilising effect, and experiments in which steam was used showed that formaldehyde is produced even when inflammation occurs. Steam and ammonia have also a protective action on the formic acid produced.

The frequent occurrence of acetaldehyde in the oxidation products, particularly when the reaction is slow, favours the view that it, and not dihydroxyethylene, is the chief intermediate product (cf. Bone and Wheeler, T., 1904, 85, 1637). On the hydroxylation theory, the scheme $\text{CH}_3\text{-CHO} \rightarrow \text{OH-CH}_2\text{-CHO} \rightarrow 2\text{CH}_2\text{O}$ is quite possible.

E. H. R.

A Solid Water-soluble Formaldehyde Preparation. ROBERT COHN (D.R.-P. 345145; from *Chem. Zentr.*, 1922, ii, 1007).—Calcium lactate is dissolved in 35% formaldehyde solution at about 90°. The white, crystalline mass obtained on cooling contains formaldehyde in the unpolymerised state and readily soluble in water. The product contains 12–14% of formaldehyde. It may be used in pharmaceutical preparations.

G. W. R.

Vapour Pressure of Acetaldehyde. ROBERT GILMOUR (*J. Soc. Chem. Ind.*, 1922, 41, 293–294r).—The author has determined the boiling point of acetaldehyde corresponding with various pressures ranging from 100 mm. to 1011 mm. of mercury, employing the method devised by Wade and Merriman (T., 1911, 99, 984; 1912, 101, 2438). The sample of acetaldehyde was synthesised from acetylene and had b. p. (constant within 0.03°) 20.55°/771 mm. The following "smoothed" values were found for the vapour pressure in mm. of mercury at the respective temperatures: 27°, 981; 25°, 911; 23°, 846; 21°, 786; 20°, 757; 19°, 729; 17°, 676; 15°, 627; 13°, 580; 11°, 534; 9°, 490; 7°, 451; 5°, 414; 3°, 378; 1°, 346; 0°, 331; -1°, 317; -3°, 290; -5°, 264; -7°, 241; -9°, 219; -11°, 200; -13°, 181; -15°, 163; -17°, 147; -19°, 132; -21°, 119; -23°, 106. The following values for the density were determined: d_4^{20} 0.8058; d_4^{25} 0.7839. The value of the latent heat of vaporisation at 20°, calculated from the results by the method of Lewis and Weber (*J. Ind. Eng. Chem.*, 1922, 14, 486), was 132 cal. per gram. The corresponding value of Trouton's constant is 19.8.

J. S. G. T.

The Reverse Pinacolin Transformation. BEETIL NYBERGH (*Hyllningsskrift tillägnad Ossian Aschan*, 1920, 98–102).—When

heated with anhydrous oxalic acid, pinacolyl alcohol yields a neutral ester, m. p. 24° , b. p. $130^{\circ}/8$ mm., $252^{\circ}/760$ mm., d_4^{20} 0.9433, and an unstable acid ester. When heated with anhydrous oxalic acid, the esters yielded a distillate of which fractions had b. p. $65-60^{\circ}$, d_4^{20} 0.6970, n_D 1.40451, and b. p. $70-72^{\circ}$, d_4^{20} 0.7072, n_D 1.41230, respectively, an ester, b. p. $125-127^{\circ}$, of unknown constitution, and an unsaponifiable product, b. p. $180-200^{\circ}/8$ mm. Transformation temperatures were determined as follows: (1) pinacolyl alcohol and 5 mols. of anhydrous oxalic acid, 105° ; (2) acid oxalic acid ester (dissociation temperature 133°) and 4 mols. of oxalic acid, 105° ; (3) neutral oxalic acid ester and 4.5 mols. of oxalic acid, no transformation even at 135° . CHEMICAL ABSTRACTS.

Permeability of the Glomerulus Membrane for Isomeric Sugars. H. J. HAMBURGER (*Klin. Woch.*, 1922, **4**, 418; from *Chem. Zentr.*, 1922, **1**, 895).—Whilst the glomerulus membrane is impermeable to dextrose, it is permeable to fructose, mannose, and *l*-glucose. Experiments with a number of isomeric sugars showed that in some cases permeability is partial. The partial retention of *d*-galactose is held to be due to its occurrence in aqueous solution in two forms, one of which is retained and the other passed by the membrane. Quantitative separation of isomeric sugars by means of the glomerulus membrane was effected in the case of mixtures of dextrose and fructose and of dextrose and lactose.

G. W. R.

The Preparation of Lævulose. T. SWANN HARDING (*J. Amer. Chem. Soc.*, 1922, **44**, 1765—1768).—A solution of sucrose (2000 grams) in water (6000 c.c.) is acidified with glacial acetic acid (2 c.c.) and treated with such a quantity of invertase that hydrolysis is complete in about eighteen hours at $20-30^{\circ}$, the end of the reaction being judged by the initial and final polarimeter readings of the solution. A few grams of active decolorising carbon are added, and the solution is filtered. The clear, colourless filtrate is immediately concentrated in a vacuum to a syrup of about 90—95% total solids, care being taken to effect the operation at as low a temperature as is possible by the use of a good water pump. The thick syrup is mixed with two volumes of hot glacial acetic acid, cooled, seeded with dextrose, and allowed to crystallise at $15-20^{\circ}$ during three or four days. The dextrose is removed and washed thoroughly with glacial acetic acid; its weight should be 36—37.5% of that of the sucrose taken. The filtrate is diluted with two volumes of distilled water and concentrated to a thin syrup in a vacuum at a low temperature. The resulting thin syrup is again diluted with water and subsequently concentrated at a low temperature until it contains about 90—95% of total solids. The final syrup is mixed with an equal volume of hot glacial acetic acid, the mixture cooled somewhat, seeded with lævulose, and allowed to remain at $15-20^{\circ}$, crystallisation being usually complete in two or three days. The crystals are removed and washed with glacial acetic acid. The yield of crude sugar is 23.5—28% of the

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weight of sucrose taken. Further purification is effected by dissolving the crude product (400 grams) in boiling ethyl alcohol (75%, 200 c.c.), adding absolute ethyl alcohol (300 c.c.) and decolorising with active carbon. The filtered solution is diluted further with absolute ethyl alcohol (100 c.c.), seeded with laevulose, and allowed to crystallise in a desiccator at the atmospheric temperature. The yield is 75–80% of the weight of crude sugar taken. Generally, a second crystallisation by the same method is necessary for the production of a pure material.

H. W.

The Action of Hydrogen Peroxide on Pure Solutions of Dextrose, Lævulose, Sucrose, Lactose, and Maltose. C. W. SCHONEBAUM (*Rec. trav. chim.*, 1922, **41**, 503–508).—Previous workers on this subject appear to have obtained contradictory results. The author finds that hydrogen peroxide in dilute solution has practically no action on sugars, with the exception of sucrose, even when heated at 70°. At this temperature, sucrose undergoes partial inversion; this, however, does not occur if the solution is slightly alkaline. Sugars are decomposed by concentrated solutions of hydrogen peroxide.

H. J. E.

Crystalline Glucose-ammonia and isoGlucosamine. ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI (*T.*, 1922, **121**, 1682–1688).

Crystalline Salts of some Physiologically Important Sugar Phosphates. C. NEUBERG and O. DALMER (*Biochem. Z.*, 1922, **131**, 188–192).—The salts of the phosphoric esters of the sugars prepared hitherto have been amorphous. By use of the alkaloids, crystalline salts can be obtained. The following are described. *Di-strychnine hexosemonophosphate* crystallises with 5H₂O, has no characteristic m. p., and gives $[\alpha]_D^{25} = -30.8^\circ$ in 50% alcohol. The *barium* salt regenerated from this has $[\alpha]_D^{25} + 2.89^\circ$. *Di-brucine hexose-monophosphate* crystallises with 9H₂O and decomposes about 160°. It has $[\alpha]_D^{25} = -26.85^\circ$ in 20% alcohol. The *cinchonidine* salt has also been prepared. *Di-strychnine hexose-diphosphate* crystallises with 2H₂O and has $[\alpha]_D^{25} = 20.4^\circ$ in 65% alcohol. *Di-strychnine sucrose-monophosphate* crystallises with 6H₂O, but shows no rotation. It is prepared from Merck's calcium saccharophosphate (hesperonal-calcium).

H. K.

The Inversion of Sucrose by Alkaline Copper Solution. L. MAQUENNE (*Bull. Soc. chim.*, [iv], 1922, **31**, 799–806; cf. A., 1916, ii, 56, 156, and 202).—The author refers to his previous work on this subject and points out that Canals (this vol., ii, 592) has obtained incorrect results in ignoring this work. He repeats, with examples, the details of the method and technique developed by him.

H. J. E.

The Constitution of the Disaccharides. VI. The Biose of Amygdalin. WALTER NORMAN HAWORTH and GRACE CUMMING LEITCH (*T.*, 1922, **121**, 1921–1929).

The Action of Ozone on Pure Solutions of Maltose. C. W. SCHONEBAUM (*Rec. trav. chim.*, 1922, **41**, 501—502; cf. this vol., i, 223, 717).—Three hours' ozonisation of a 5% solution of maltose effects no decomposition even at 70°; in 0.1N-acid solution, no change occurs at the ordinary temperature, but rapid inversion takes place at 70°. In 0.1N-alkali solution, about 35% of the sugar is decomposed at the ordinary temperature, whilst at 70° it is rapidly destroyed, although complete decomposition requires considerable time. The products are similar to those in the other cases which have been studied, namely, water and carbon dioxide, with formic acid as an intermediate substance. H. J. E.

Pentosans. EMIL HEUSER (*J. pr. Chem.*, 1922, [iii], **104**, 80).—A reference to a paper of Salkowski (this vol., i, 323) bearing on the author's work (cf. this vol., i, 113). W. O. K.

Combination of Iodine and Starch. I. HANS VON EULER and STIG BERGMAN (*Kolloid Z.*, 1922, **31**, 81—89).—With the object of ascertaining the nature of the blue substance formed between soluble starch and iodine, the authors have carried out a number of partition experiments between a benzene solution of iodine and water, potassium iodide solution, 1% soluble starch solution, and starch solution containing various amounts of potassium iodide, respectively, at 6°, 15°, and 30°. It is shown that aqueous solutions of soluble starch dissolve more iodine than pure water and that the solubility of iodine in starch solutions containing potassium iodide is greater than the sum of the solubilities in starch solution and an aqueous solution of potassium iodide. That is, the power of starch to take up iodine is increased by the presence of potassium iodide. The absorption spectra of starch solution, starch iodide solution, and mixtures of these two respectively with various amounts of potassium iodide have been measured. The results show that there is a considerable displacement of the absorption of starch iodide by potassium iodide. The absorption is increased in the blue region by the addition of potassium iodide, and thereby the solution takes on a red colour. J. F. S.

Combination of Iodine and Starch. II. HANS VON EULER and STURE LANDERGREN (*Kolloid Z.*, 1922, **31**, 89—90; cf. preceding abstract).—The partition of iodine between starch solutions and a toluene solution of iodine has been investigated with the object of ascertaining the influence of the quantity of starch on the amount of iodine taken up by the starch. In all cases, soluble starch was employed. The results show that in solutions of varying concentrations of starch (0.27—1.9%) and constant concentration of potassium iodide (0.001N) the amount of iodine extracted from toluene solutions of iodine (1—8 gram per 100 c.c. of toluene) does not increase with increasing concentration of starch. J. F. S.

Plant Colloids. XIII. Synthetic Amylo-phosphoric Acids. M. SAMEC and ANKA MAYER (*Koll. Chem. Beihefte*, 1922, **16**, 89—98).—It is shown that when the erythroamyloses from the starch grains are esterified with phosphoric acid, a product

which corresponds in all points with amylopectin is obtained. By a similar treatment, the amyloamyloses are converted into a jelly-forming substance analogous to amylopectin. The iodine colour of these phosphorus-containing substances is the same as that of the starting materials, provided that during the esterification no fundamental change of the basal substance has taken place. The power of colouring with iodine is therefore to a large extent independent of the degree of hydration and the degree of association of the substance. The contradictory statements regarding the iodine colour of amylopectin are brought into line, and it is shown that a comparison of the phosphorus-containing starch hydrocarbons furnishes information with respect to the formation of jellies.

J. F. S.

Chemistry of the Manufacture of Artificial Silk. K. HESS (*Textilber. Wiss. Ind. Handel*, 1922, **3**, 41—46; from *Chem. Zentr.*, 1922, i, 738—739).—In the dissolution of cellulose by copper oxide-ammonia, the cellulose is supposed to be depolymerised to a simpler compound which combines with copper. On precipitation, the copper forms a normal salt, whilst the cellulose constituent polymerises by virtue of its residual affinity. By the action on cotton of acetyl chloride saturated with hydrogen chloride, the acetyl compound of a depolymerisation product of cellulose is obtained. It is probable that two molecules of this are combined in the cellulose molecule. A constitutional formula for cellulose is given.

G. W. R.

Saccharification of Cellulose. P. P. BUDNIKOV and P. V. ZOLOTAREV (*Bull. Inst. Polyt. Ivanovo-Voznesensk*, 1921, **4**, 119—128).—When dry filter-paper is saccharified by treating it with cold 72% sulphuric acid, then diluting the transparent solution obtained until it contains only 3% of acid, and heating this in an autoclave at 120° for two hours, the percentage of dextrose in the resulting liquid does not exceed 0.6. The concentration of the sugar may, however, be increased by diluting the strongly acid solution, not with water, but with dextrose solution previously obtained in the same way and freed from sulphuric acid. When a solution containing 1% of dextrose and 3% of sulphuric acid is introduced into the cathode chamber of an electrolytic cell and the anode chamber, separated by means of a porous pot, is charged with water acidified with sulphuric acid, electrolysis should result in the collection of all the acid in the anode chamber; with a suitable porous pot, as much as 91.5% of the acid was separated by this method.

T. H. P.

Cellulose Nitrate. A. ANGELI (*Z. ges. Schiess. u. Sprengstoffw.*, 1922, **17**, 113—115).—The action of pyridine on collodion-cotton (12% nitrogen) was studied with the object of elucidating the changes undergone by the basic organic stabilisers usually added to cellulose nitrate and glyceryl nitrate powders. The nitro-cotton was extraordinarily easily gelatinised by the pyridine,

forming a very viscous liquid, which, however, rapidly lost its viscosity and in a few days had the appearance of ordinary pyridine. On adding water to the solution, a white, resinous mass was precipitated, which tenaciously retained the odour of pyridine even after solution in sulphuric acid. The white powder obtained comprised 80% of the original nitro-cotton, was easily soluble in acetic acid, soluble in alcohol, but almost insoluble in ether and in benzene. The substance burnt much more slowly than the original nitro-cotton. Its nitrogen content varied between 9% and 10%, and it was similar to the product obtained by Berl and Fodor (A., 1911, i, 264) by the action of alkali hydroxides or carbonates on very dilute solutions of cellulose nitrate in alcohol and ether. When heated in a glass tube, the substance began to go brown at 165°, and became almost black at 250°. An alcoholic solution of the substance when poured into water gave a very stable, opalescent, colloidal solution, which was coagulated by sodium chloride, ammonium sulphate, or gelatin, but gave no precipitate with aqueous tannin. With benzene and sulphuric acid, nitrobenzene was produced, whilst sulphuric acid and mercury caused an evolution of nitrogen tetroxide. A small quantity of the solution poured on to a test-paper saturated with dimethylaminoazobenzene gave after a short time an intense red colour. The colloidal solution is insoluble in ammonia, but easily soluble in alkali hydroxides, the solution giving a voluminous white precipitate with acids. Ammoniacal silver nitrate is reduced by the colloidal solution, but Fehling's solution is almost unaffected. The substance reacts readily with phenylhydrazine. The development of acidity is ascribed either to the volatilisation of the pyridine or to hydrolysis of a pyridine salt.

H. C. R.

Copper Salts of Aminosulphonic Acids. MARCEL DELÉPINE and RENÉ DEMARS (*Bull. Sci. Pharmacol.*, 1922, 29, 14—20; from *Chem. Zentr.*, 1922, i, 634).—An investigation of the formation of complex salts of copper with amino-acids. Dimethylamino-sulphonic acid forms a simple *copper* salt, $[\text{Me}_2\text{N}\cdot\text{SO}_3]_2\text{HCu}\cdot 5\text{H}_2\text{O}$, light blue crystals. The *nickel* salt, $[\text{Me}_2\text{N}\cdot\text{SO}_3]_2\text{Ni}$, forms small, bluish-green crystals, m. p. 128—129°. Neither of these is a complex salt. The *acid* potassium hydrogen salt of aminomethane-disulphonic acid gives a *copper* salt, $[\text{NH}_2\cdot\text{CH}(\text{SO}_3\text{K})\cdot\text{SO}_3]_2\text{Cu}$, of deeper blue colour than copper sulphate but of lighter blue than copper salts of α -amino-acids. The *nickel* salt is pale blue. Among the β -amino-acids, taurine has no action on cuprous oxide. Phenyltaurine dissolves cuprous oxide, giving a greenish-blue colour which soon changes to red and brown. Phenylmethyltaurine and phenylethyltaurine, also, do not give copper salts of constant composition.

G. W. R.

Syntheses of Alkylidenecyanoacetic Acids and of Substituted Succinic Acids. I. Acids containing Aromatic Residues. ARTHUR LAPWORTH and JOHN ALEXANDER MCBAE (*T.*, 1922, 121, 1699—1712).

The Preparation of Methylguanidine, and of $\beta\beta$ -Dimethylguanidine by the Interaction of Dicyanodiamide, and Methylammonium and Dimethylammonium Chlorides Respectively. EMIL ALPHONSE WERNER and JAMES BELL (T., 1922, **121**, 1796—1794).

The Formation of Bromine Derivatives of Carbon Compounds without the Production of Hydrogen Bromide. BIRAJ MOHAN GUPTA and JOCELYN FIELD THORPE (T., 1922, **121**, 1896—1904).

Butenonitriles. II. P. BRUYLANTS (*Bull. Soc. chim. Belg.*, 1922, **31**, 225—230; cf. this vol., i, 817).—Vinylacetonitrile reacts readily with alcohols, yielding β -alkoxybutyronitriles, when a trace of the corresponding sodium alkoxide is present. In the case of the lower alcohols, the yield is diminished by reason of the polymerisation of the nitrile. The additive products, of the general formula $OR\cdot CHMe\cdot CH_2\cdot CN$, are colourless liquids of pleasant odour; the following have been prepared: β -methoxybutyronitrile, b. p. 169—170°/759 mm.; d_4^{20} , 0.91643; $n_{D,20}^{20}$, 1.40664; $n_{D,15}^{20}$, 1.40938; $n_{D,10}^{20}$, 1.41363; β -ethoxybutyronitrile, b. p. 175.5—176.5°/764.7 mm.; d_4^{20} , 0.89164; $n_{D,20}^{20}$, 1.40814; $n_{D,15}^{20}$, 1.41076; $n_{D,10}^{20}$, 1.41537; β -propoxybutyronitrile, b. p. 192—193°/766.5 mm.; d_4^{20} , 0.88312; $n_{D,20}^{20}$, 1.41183; $n_{D,15}^{20}$, 1.41443; $n_{D,10}^{20}$, 1.41908; β -isopropoxybutyronitrile, b. p. 182—183°/764.2 mm.; d_4^{20} , 0.87408; $n_{D,20}^{20}$, 1.40994; $n_{D,15}^{20}$, 1.41235; $n_{D,10}^{20}$, 1.41759; β -allyloxybutyronitrile, b. p. 196—198°/768 mm.; d_4^{20} , 0.90165; $n_{D,20}^{20}$, 1.42176; $n_{D,15}^{20}$, 1.42441; $n_{D,10}^{20}$, 1.42935; β -butoxybutyronitrile, b. p. 209.5—210.5°/757.5 mm.; d_4^{20} , 0.87785; $n_{D,20}^{20}$, 1.41765; $n_{D,15}^{20}$, 1.41961; $n_{D,10}^{20}$, 1.42474; β -isobutoxybutyronitrile, b. p. 201—201.5°/763.5 mm.; d_4^{20} , 0.86876; $n_{D,20}^{20}$, 1.43123; $n_{D,15}^{20}$, 1.41573; $n_{D,10}^{20}$, 1.42073. An attempt to prepare the phenol derivative was not successful, leading to the formation of a mixture of the two crotononitriles from the vinylacetonitrile; the author states that this is due to the formation of an additive product and its subsequent decomposition. The action of concentrated sulphuric acid on the nitrile results in the formation of isocrotonic acid, and the mechanism of the reaction is discussed. H. J. E.

Optically Active Diazo-compounds. II. H. M. CHILES and W. A. NOYES (*J. Amer. Chem. Soc.*, 1922, **44**, 1798—1810).—In a previous communication (Marvel and Noyes, A., 1921, i, 13), an account has been given of unsuccessful experiments undertaken in the hope of preparing optically active aliphatic diazo-compounds in which the only asymmetric carbon atom is combined with the two nitrogen atoms. Subsequently, Levene and Mikeska (A., 1921, i, 233) have described optically active ethyl diazsuccinate. Six such active compounds have now been prepared. The failure of former experiments is due to the fact that such compounds racemise very easily; it is necessary to carry through all operations very carefully and to distil the compounds under a very low pressure.

Ethyl d-glutamate hydrochloride, m. p. 96—98°, is dissolved in

water and the solution is mixed with sodium acetate, sodium nitrite, and ether and diazotised at -10° by the gradual addition of sulphuric or acetic acid. The product, which is a mixture of the corresponding diazo- and hydroxy-esters, is treated with a quantity of sodium methoxide dissolved in ether and methyl alcohol sufficient to unite with the hydroxy-ester, and the diazo-ester is subsequently distilled under greatly diminished pressure. As thus obtained, *ethyl α -diazoglutarate* has b. p. $92-93^{\circ}/0.1$ mm., $[\alpha]_D +0.87^{\circ}$ to $+1.68^{\circ}$. Hydrolysis of the optically active ester by dilute sulphuric acid gives an optically active product which is probably a mixture of ethyl glutaconate and ethyl 5-ketotetrahydrofuran-2-carboxylate. Saponification of the products of the hydrolysis of the diazo-ester yields an optically active sodium salt which rotates in the same direction as the original amino-acid. When the sodium salt is acidified and the mixture extracted with ether, the ethereal extract is optically active in the same sense as the original amino-acid. Ethyl *d*-diazoglutarate is reduced by aluminium amalgam in the presence of moist ether and the product is hydrolysed by acid to glutamic acid, the rotation of which is about 13% of that of the pure substance.

Ethyl *d*-glutamate is converted at $160-170^{\circ}/20$ mm. into ethyl 5-pyrrolidone-2-carboxylate, m. p. 54° after softening at $49-50^{\circ}$, $[\alpha]_D -2.45^{\circ}$ in aqueous solution (cf. Fischer and Bochner, A., 1911, i, 485).

Methyl d-glutamate hydrochloride, which could not be caused to solidify, is converted in a similar manner into *methyl α -diazoglutarate*, b. p. $86-87^{\circ}/0.5$ mm., $85-86^{\circ}/0.4$ mm., $82-83^{\circ}/0.2$ mm., $d_4^{20} 1.185$, $n_D^{20} 1.4753$, $[\alpha]_D^{20} +0.89^{\circ}$.

isoPropyl d-glutamate, a colourless, viscous liquid, b. p. $115-117^{\circ}/0.15$ mm., $d_4^{20} 1.023$, $n_D^{20} 1.4402$, $[\alpha]_D^{20} +5.08^{\circ}$ (the *hydrochloride* is non-crystalline) is transformed by nitrous acid into *isopropyl α -diazoglutarate*, $[\alpha]_D +1.24^{\circ}$, which could not be distilled without decomposition: the crude material is hydrolysed by sulphuric acid (20%) to *isopropyl α -hydroxyglutarate*, $n_D^{20} 1.4440$, $[\alpha]_D^{20} +1.12^{\circ}$ in ethereal solution.

An attempt to prepare *n*-butyl *d*-glutamate resulted in the production of *n*-butyl 5-pyrrolidone-2-carboxylate, a colourless liquid, b. p. $151-153^{\circ}/0.2$ mm., $d_4^{20} 1.1101$, $n_D^{20} 1.4773$, $[\alpha]_D^{20} -12.39^{\circ}$.

Ethyl *L*-aspartate hydrochloride, m. p. 95° , is converted by nitrous acid into ethyl α -diazosuccinate, b. p. $77-78^{\circ}/0.1$ mm., $d_4^{20} 1.139$, $n_D^{20} 1.4620$, $[\alpha]_D^{20} -1.23^{\circ}$. When hydrolysed with dilute sulphuric acid, it gives a product which has $[\alpha]_D^{20} -0.98^{\circ}$ in ethereal solution.

Ethyl *L*- α -amino-*n*-hexoate hydrochloride (cf. Noyes and Marvel, *loc. cit.*) is converted into *ethyl L- α -diazo-*n*-hexoate*, b. p. $54-55^{\circ}/0.35$ mm., $n_D^{20} 1.4543$, $d_4^{20} 0.974$, $[\alpha]_D^{20} -1.92^{\circ}$ when dissolved in anhydrous ether. When hydrolysed with dilute sulphuric acid, it gives a levorotatory product from which a levorotatory sodium salt is obtained after treatment with sodium hydroxide. The aqueous solution of the latter, when acidified, and extracted with ether, yields a levorotatory ethereal extract. *Ethyl d- α -diazo-*n*-hexoate*,

b. p. 54—55°/0.35 mm., d_4^{20} 0.97, n_D^{20} 1.453, $[\alpha]_D^{20}$ +1.84° in dry ethereal solution, is prepared similarly from ethyl *d*-α-amino-*n*-hexoate hydrochloride.

Ethyl α-diazoisohexoate, prepared from ethyl *l*-α-aminoisohexoate hydrochloride, has b. p. 49—50°/0.50 mm., d_4^{20} 0.961, n_D^{20} 1.433, $[\alpha]_D^{20}$ -1.52° in ethereal solution.

The production of partly active hydroxy-esters by the treatment of diazo-esters with dilute acids together with the formation of partly active amino-esters by their reduction may indicate the existence of two forms of diazo-ester, possibly corresponding with the compounds indicated by the Curtius and Angeli-Thiele formulae, respectively.

It seems impossible to reconcile the Curtius formula for active diazo-esters with the ideas of atomic structure and of non-polar valency proposed by Lewis and Langmuir. The Angeli-Thiele formula may be reconciled with these theories if it is assumed that the polar valency between an ammonium group and another atom is a definite bond located in a fixed position in the compound (cf. Noyes and Potter, A., 1915, i, 79).

H. W.

The β-Chlorovinylarsines. FREDERICK GEORGE MANN and WILLIAM JACKSON POPE (T., 1922, 121, 1754—1759).

Manufacture of Allylarsinic Acid. F. HOFFMANN-LA ROCHE & Co. (Brit. Pat. 167157).—*Allylarsinic acid*, $C_3H_5AsO(OH)_2$, colourless needles or coarse prisms, m. p. 129—130°, is prepared by treating tertiary alkali arsenites in aqueous solution and in the presence of an excess of alkali with allyl haloids. The *silver salt*, *sodium hydrogen salt* (+aq), colourless, lustrous tablets which partly melt at 87—88°, the hygroscopic *disodium salt*, and the insoluble *zinc, lead, copper, cobalt, and iron salts* are described. The acid is not precipitated by the addition of magnesia mixture or calcium chloride to its cold ammoniacal solution, but, on being heated with these reagents, it precipitates a white *magnesium or calcium salt*.

H. W.

isoPropylstannonic Acid and its Derivatives. JOHN GERALD FREDERICK DRUCE (T., 1922, 121, 1859—1863).

Preparation of cycloPropane in a Pure Condition. MAX TRAUTZ and KARL WINKLER (*J. pr. Chem.*, 1922, [ii], 104, 37—43).—*cycloPropane* is conveniently prepared by the reduction of trimethylene bromide in amyl alcohol by zinc dust at 100—115°. The gas evolved is fractionated at a low temperature in an apparatus which is described, and pure *cyclopropane* obtained with the following constants: vapour density, 1.45—1.49; d_4^{20} of liquid, 0.720; m. p. -127°; b. p. -34.5°/750 mm.; n_{He} 1.000977.

W. O. K.

Problems of Organic Chemistry. I. The Velocity of Ring Fission in Gases. Isomerisation of cycloPropane. MAX TRAUTZ and KARL WINKLER (*J. pr. Chem.*, 1922, [ii], 104, 53—79).—As no case of intermolecular change in a gas has so far been studied kinetically, measurements have been made of the

reversible reaction, propylene \rightleftharpoons cyclopropane. The mixture resulting by passing pure cyclopropane or propylene through a tube at a definite temperature of about 600° or 700° is analysed by finding the density of the product in the liquid state at -79° (cf. this vol., i, 909). The result has to be corrected for the polymerised material also formed. The equilibrium mixture consists very largely of propylene. The isomerisation of cyclopropane to propylene is unimolecular, and its speed is influenced by the shape of the vessel and the material of which it is made, although these effects decrease in magnitude with rise of temperature. The heat of the reaction at 550—650° is calculated to be 63900 cal. At higher temperatures the reaction proceeds further and carbon, methane, and hydrogen are formed from propylene. W. O. K.

Application of the Octet Theory to Single Ring Aromatic Compounds. ERNEST C. CROCKER (*J. Amer. Chem. Soc.*, 1922, 44, 1618—1630).—A theoretical paper in which the Lewis—Langmuir octet theory is considered as undergoing evolution, in that the original cubical octet has given way in certain cases to that of an octet which consists of four pairs of electrons arranged as are the points of a tetrahedron. The pairing tendency of electrons is considered as possibly due to the presence of magnetic properties in the electrons (magnetons). The Kekulé, Dewar, and centric formulae of benzene are expressed in octet nomenclature and are considered as unstable forms. A stable arrangement is deduced and shown to be applicable, not only to benzene, but also to other aromatic compounds. In this arrangement, there is a ring of six carbon atoms, each singly linked to its neighbour on either side and to hydrogen. The remaining six electrons are situated between the carbon atoms in the plane of the ring, thus forming an octet for each carbon atom. These six "aromatic" electrons are considered as being in stable equilibrium only when paired up near carbon atoms 1, 3, and 5, or 2, 4, and 6 (or oscillating between these forms in benzene itself or in derivatives containing six identical substituents). Substituents on the carbons are considered as favouring the retention of one or other grouping of electrons, according to their electrical action on the adjacent or very near electrons, resulting in ortho, meta, or para patterns. Substituents with more than five kernel charges on the octet joining the ring plus its attached hydrogens are indicated as favouring the ortho and para patterns (as in toluene and chlorobenzene), and those with five or less charges as favouring the meta pattern (as in nitrobenzene and benzaldehyde). Substitution is considered as possible only when the hydrogens are lightly held ("open" positions of the adjacent aromatic electrons). The influence of these electrons is to "open" or "close" positions according to their attractive action on the hydrogen kernels. The relative ease of substitution into the various substituted benzenes is treated as a result of polarity considerations, which are developed as an essential consequence of the octet theory, and an addition to the above-mentioned aromatic structural considerations. Preference for substitution

in ortho- or para-positions is treated in like manner. Pyridine, thiophen, furan, and pyrrole are treated similarly and afford striking confirmations of the postulated structure in their behaviour. Addition of any kind is shown to be inconsistent with the retention of the aromatic structure in the remainder of the ring. J. F. S.

Conjugation and the Structure of Benzene. MAURICE L. HUGGINS (*J. Amer. Chem. Soc.*, 1922, **44**, 1607—1617).—A theoretical paper, in which on the basis of an assumed maximum in the force-distance curves, representing the repulsion between electrons, the probable mechanisms of the simplest types of organic reactions are given and explained. As intermediary steps in these reactions, bonds of three or four or more electrons surrounded by three, four, or more atomic nuclei are assumed. The reactivity of double and triple bonds is explained on this point of view. Conjugation is briefly considered and the structure of typical compounds given, some of these being similar to those put forward by Erlenmeyer. The relationship of keto-enol tautomerism to conjugation is also discussed. When this idea of conjugation is applied to benzene, a formula of the centroid type, as proposed by Körner, is obtained. The evidence for and against this structure is briefly considered. It is shown that the objections raised against it are all invalid or inconclusive. On the other hand, the known properties of benzene and its derivatives are very adequately represented by their centroid structures. Further, recent evidence from crystal structures proves that this benzene structure is the correct one.

J. F. S.

Oxidation of o-Toluenesulphonamide. A. V. PAMELOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk*, 1921, **4**, 167—168).—In the oxidation of o-toluenesulphonamide to o-benzoic sulphimide ("saccharin") by means of potassium permanganate, the yield obtained is increased by 10—15% and the proportion of permanganate required diminished by nearly 50% if the alkali salt of the sulphonamide is used instead of the free sulphonamide. Electrolytic oxidation of the sulphonamide (Chemische Fabrik vormals von Heyden, D.R.-P. 85491), like that of p-toluenesulphonic acid (Sebor, A., 1903, i, 554), gives unsatisfactory results.

T. H. P.

The Formation of Derivatives of Tetrahydronaphthalene from γ -Phenyl Fatty Acids. II. ARNOLD STEVENSON and JOCELYN FIELD THORPE (*T.*, 1922, **121**, 1717—1722).

Absorption of Ultra-violet Rays by Naphthalene. VICTOR HENRI and PIERRE STEINER (*Compt. rend.*, 1922, **175**, 421—423).—A quantitative measurement of the absorption of solutions of naphthalene in hexane, ethyl ether, alcohol, and water reveals seventeen bands between $\lambda=3207$ and $\lambda=2563$ and one band in the extreme ultra-violet at $\lambda=2209$. The absorption curve of naphthalene is displaced towards the red with respect to that of benzene, and its absorption is more than ten times as strong as that of benzene. The frequencies of the naphthalene bands present

a double periodicity which corresponds with the fundamental intervals $a=921$ and $b=159$. The influence of the solvent on the spectrum of naphthalene is the same as in the case of benzene.

W. G.

Triphenylmethyl. XXX. Diphenyl- β -naphthylmethyl and the Colour of Free Radicles. M. GOMBERG and F. W. SULLIVAN, jun. (*J. Amer. Chem. Soc.*, 1922, **44**, 1810-1833).—Diphenyl- β -naphthylmethyl has been isolated in the crystalline state. The conductivity of the free radicle has been examined in sulphur dioxide and the conductivities of the chlorides and bromides of triphenylmethyl, diphenyl- α -naphthylmethyl, and diphenyl- β -naphthylmethyl have been determined in both sulphur dioxide and hydrogen cyanide. The results show that the property of electrolytic dissociation is general for this class of compound. The bromides give strongly conducting solutions with but little difference between the conductivities of the individuals. The chlorides are not such good conductors, and there is a variation among them. The conductivities of the chlorides are related in the same way as the dissociation of the corresponding free radicles, the order of diminishing conductivity being, diphenyl- α -naphthylmethyl chloride, diphenyl- β -naphthylmethyl chloride, and triphenylmethyl chloride. The latter has a large negative temperature coefficient of conductivity. The same relationship holds for the free radicles; diphenyl- β -naphthylmethyl is a better conductor than triphenylmethyl. The conductivity of the triarylmethyl haloids in hydrocyanic acid is uniformly greater than in sulphur dioxide. The bromides show molecular conductivities comparable to that of an aqueous solution of potassium hydroxide, or about twice the conductivity of the alkali haloids in water. The molecular weight of diphenyl- β -naphthylmethyl has been determined in carbon tetrachloride, ethylene chlorobromide, benzene, nitrobenzene, cyclohexane, *p*-bromotoluene, *p*-dichlorobenzene, and naphthalene, the freezing points of which cover the range -22° to $+80^{\circ}$. It is found that the hexa-arylethane is dissociated from 15% to 50%.

The effect of change in concentration of the free radicle on the dissociation and colour of the solutions has been examined. The resulting changes in colour intensity are independent of the changes in dissociation. Also the changes in colour intensity which result from variations in temperature are not parallel to the changes in dissociation which are thus produced. These facts point to the conclusion that the development of colour in solutions of free radicles is not due entirely to dissociation of the hexa-arylethane into the triarylmethyl. The most satisfactory explanation of the facts is in the hypothesis that, in addition to dissociation, there is also tautomerisation of the benzenoid triarylmethyl into the quinonoid form. The equilibrium between the bimolecular and unimolecular forms on the one hand, and that between the two unimolecular tautomerides on the other, are not equally influenced by changes either in concentration or in temperature.

Diphenyl- β -naphthylcarbinol, colourless crystals, m. p. 117.5° ,

is most conveniently prepared by the action of magnesium phenyl bromide on ethyl β -naphthoate in the presence of boiling toluene. It is reduced by zinc dust and acetic acid to diphenyl- β -naphthylmethane, m. p. 77–78°, which has properties differing from those described to it by Lehne (A., 1880, 478). *Diphenyl- β -naphthylmethyl chloride*, m. p. 94.5°, is prepared in almost quantitative yield by saturating an ethereal solution of the carbinol with hydrogen chloride in the presence of calcium chloride; it gives red additive products with stannic and mercuric chlorides. It is converted by an alcoholic solution of sodium ethoxide into *diphenyl- β -naphthylmethyl ethyl ether*, colourless crystals, m. p. 114°. *Diphenyl- β -naphthylmethyl anilide* has m. p. 158.5°. *Diphenyl- β -naphthylmethyl bromide*, colourless crystals, m. p. 136°, is prepared by the addition of acetyl bromide to a solution of the carbinol in benzene. *Diphenyl- β -naphthylmethyl*, a colourless or pale yellow, finely divided, crystalline powder, m. p. 135–140° to a red liquid, is obtained by the action of molecular silver on a solution of diphenyl- β -naphthylmethyl chloride in carbon disulphide. It appears to form an additive compound with methyl butyl ketone. It is transformed by oxygen into the corresponding *peroxide*, colourless crystals, m. p. 166°, the yield being 72% of that theoretically possible when an ethereal solution of the radicle is used, but only 46% in the presence of benzene as solvent. The free radicle is not very sensitive to light. It reacts with iodine in accordance with the scheme $2\text{C}_{10}\text{H}_7\text{CPh}_2 + \text{I}_2 \rightarrow 2\text{C}_{10}\text{H}_7\text{CPh}_2\text{I}$, but an equilibrium is attained before the change has proceeded to completion. H. W.

Metachromism of Toluidine-blue. ROBERT SCHWARZ and ERIKA HERRMANN (*Kolloid Z.*, 1922, **31**, 91–94).—The colloidal chemical properties of toluidine-blue have been investigated with the object of explaining the metachromatic behaviour of this substance. On diffusion of 0.2 to 0.002% solutions, it is found that separation into two diffusion zones takes place with velocities of 6 mm. and 9 mm., respectively, per twenty-four hours. The 9 mm. zone is considerably lighter in colour than the 6 mm. zone. The formation of the two zones is confirmed by ultrafiltration measurements, and both sets of results indicate that solutions of toluidine-blue constitute a polydisperse system which contains both colloidal as well as molecular disperse particles. Transport experiments bring about a separation, the cathode region becoming reddish-blue in colour and the anode pure blue. The behaviour of solutions of toluidine-blue with various colloidal substances has been examined. Thus α -silicic acid gel is coloured blue, whilst the β -gel is coloured red. Similar results were obtained with the various preparations of stannic acid, barium sulphate, aluminium hydroxide, and magnesium ammonium phosphate. The results all point to the one conclusion, namely, that the metachromism of toluidine-blue is due in the first place to the difference in the degree of dispersion of the adsorbent and in the second place to the electrical condition of the adsorbing surface, which is determined by the nature of the ions adsorbed on the surface. J. F. S.

The Condensation of Phenols with the Hydrochlorides of Cyanamides and Carbodi-imides, and its Relation to the Hoesch Reaction. WALLACE FRANK SHORT and JOHN CHARLES SMITH (T., 1922, **121**, 1803—1808).

The Solubility and Volatility of 3 : 5-Dinitrophenol. NEVIL VINCENT SIDGWICK and THOMAS WESTON JOHNS TAYLOR (T., 1922, **121**, 1853—1859).

The Migration of Acyl from Nitrogen to Oxygen. L. CHAS. RAIFORD and JOHN R. COUTURE (*J. Amer. Chem. Soc.*, 1922, **44**, 1792—1798).—In continuation of previous work (Raiford, A., 1920, **156**), it is shown that, when the acetyl and benzoyl radicles are introduced into the *o*-aminophenols obtained from *o*- and *m*-cresol, respectively, the benzoyl radicle is found attached to nitrogen in each case, regardless of the order of introduction, thus confirming the observations reported previously.

o-Cresol is converted by bromine into 5-bromo-*o*-cresol, and the latter is converted by sodium nitrite and glacial acetic acid into 5-bromo-3-nitro-*o*-cresol, m. p. 90.5°, which appears to be the sole product of the change. The nitro-compound is reduced by Raiford's method (A., 1911, i, 993) to 5-bromo-3-amino-*o*-cresol hydrochloride. This substance is converted by acetic anhydride and fused sodium acetate into 4-bromo-2-acetyl-amino-*o*-tolyl acetate, pale brown, silky needles, m. p. 200°, which is slowly dissolved by aqueous sodium hydroxide solution with the formation of 4-bromo-2-acetyl-amino-*o*-cresol, colourless needles, m. p. 119°. Benzoylation of the latter compound with benzoyl chloride and sodium hydroxide gives 4-bromo-2-benzoyl-amino-*o*-tolyl acetate, slender, colourless needles, m. p. 168°, the constitution of which is established by the observation that it is hydrolysed by aqueous sodium hydroxide solution to 4-bromo-2-benzoyl-amino-*o*-cresol, rose-coloured needles, m. p. 194.5°, which is also formed by the action of benzoyl chloride in an ethereal solution of 5-bromo-3-amino-*o*-cresol. Acetylation of 4-bromo-2-benzoyl-amino-*o*-cresol with sodium acetate and an excess of acetic anhydride gives 4-bromo-2-benzoyl-amino-*o*-tolyl acetate, m. p. 167° (see above).

6-Bromo-4-nitro-*m*-cresol (cf. Raiford and Leavell, A., 1914, i, 964) is reduced to the corresponding amine hydrochloride which is converted by sodium acetate and acetic anhydride into 6-bromo-4-acetyl-amino-*m*-tolyl acetate, colourless leaflets, m. p. 188°. The action of aqueous sodium hydroxide on the latter compound leads to the formation of 6-bromo-4-acetyl-amino-*m*-cresol, almost colourless needles, m. p. 199° (decomp.), which is transformed by benzoyl chloride in the presence of sodium hydroxide into 6-bromo-4-benzoyl-amino-*m*-tolyl acetate, slender, colourless needles, m. p. 157—158°. The constitution of the latter substance is established by the observation that 6-bromo-4-amino-*m*-cresol is transformed by benzoyl chloride in dry ethereal solution into 6-bromo-4-benzoyl-amino-*m*-cresol, almost colourless leaflets, m. p. 223° (decomp.), which is converted by anhydrous sodium acetate and acetic

anhydride into 6-bromo-4-benzoylamino-*m*-tolyl acetate, identical with the product described above. H. W.

Separation of Volatile Substances from Gases which are Absorbed with Difficulty. II. Use of Cresols. E. BERL and W. SCHWEBEL (*Z. angew. Chem.*, 1922, **35**, 189—192; cf. *ibid.*, 1921, **34**, 278, 369, 377).—Mixtures of cresol with ethyl ether, ethyl alcohol, and acetone give lower vapour tension values than the pure compounds; moreover, heat is developed when the substances are mixed; it is therefore concluded that molecular compounds are formed. In the case, however, of benzene and carbon tetrachloride (and therefore of hydrocarbons and chlorinated hydrocarbons in general), no such reduction of vapour tension takes place. The formation of molecular compounds, as detected by vapour tension measurements, does not take place between anisole and ethyl ether, ethyl alcohol, and acetone. A. A. E.

Formation of Additive Products between Cresols on the One Hand and Ethyl Ether, Ethyl Alcohol, Acetone, Benzene, etc., on the Other. C. and W. VON RECHENBERG (*Z. angew. Chem.*, 1922, **35**, 397—398).—As mixtures of cresols with ethyl ether, ethyl alcohol, acetone, carbon tetrachloride, benzene, and other volatile solvents, give perfectly smooth viscosity curves, which show no maxima, and the vapour-pressure curves likewise show no minima, the authors conclude that, contrary to the opinion of Berl and Schwebel (preceding abstract), no molecular additive compounds can be formed between these substances. G. F. M.

Additive Products between Cresols and Alcohols, etc. E. BERL and W. SCHWEBEL (*Z. angew. Chem.*, 1922, **35**, 398).—A reply to von Rechenberg (preceding abstract).

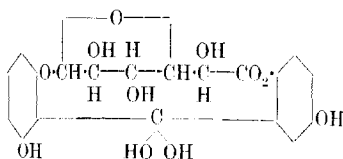
The authors maintain their view that molecular compounds are actually formed between cresols and ethyl alcohol or ether, and acetone; a vapour-pressure minimum is not necessarily to be expected when molecular compounds are formed. Further, the formation of molecular compounds does not necessarily cause a maximum in the viscosity curve, as the viscosity of the compound may be less than that of its components. G. F. M.

Chlorination of Quinol. ALFRED ECKERT and RUDOLF ENDLER (*J. pr. Chem.*, 1922, [ii], **104**, 81—84).—The chlorination of quinol in acetic acid yields a mixture of tetrachloroquinol, m. p. 226°, and 2 : 3-dichloroquinol, m. p. 143—145°, and a small quantity of 2 : 5-dichloroquinol, m. p. 165—168°. By chlorination in chloroform solution, 5 grams of 2 : 5-dichloroquinol may be obtained from 10 grams of quinol. W. O. K.

Researches on Residual Affinity and Co-ordination. IX. Cobaltammine Salts of the Nitro-Dyes. (GILBERT T. MORGAN and HERBERT JOSEPH SEYMOUR KING (*L.*, 1922, **121**, 1723—1729)).

The Precursor of Indian-yellow. K. GORTER (*Bull. Jard. bot. Buitenzorg.*, 1922, [iii], **4**, 260—267).—Euxanthogen, the substance isolated by Wichowsky from the leaves of *Mangifera indica*

(cf. van Scherpenberg, A., 1916, i, 321), is preferably named *mangiferin*. The author has confirmed Wiechowsky's formula, $C_{19}H_{18}O_{11}$, whence the substance is isomeric with euxanthic acid, to which it gives rise in the organism. The precursor is best prepared from the bark, which is first exhausted with light petroleum and then with 60% alcohol, the latter giving a yield of 2.5% on evaporation. The leaves yield somewhat less readily 1.7%. The substance forms thin, pale yellow needles, m. p. 271° , $[\alpha]_D^{25} + 32.8^\circ$; unlike euxanthic acid, the substance does not at once liberate carbon dioxide from sodium hydrogen carbonate solution, whence the author concludes that it contains no carboxyl group. Ferric chloride gives in alcoholic solution a green coloration. Fehling's solution is reduced on prolonged heating, Bial's reagent gives a green colour. Diazomethane yields a *dimethyl* ether, $C_{19}H_{18}O_9(OMe)_2$, m. p. 276° . Mangiferin crystallises from dilute alcohol with $3H_2O$, of which $1H_2O$ is lost on exposure to air and the rest at 110° in a vacuum. It yields an amorphous *hepta-acetyl* derivative, $C_{19}H_{11}O_{11}(OAc)_7$, m. p. about 150° . Euxanthic acid under the same conditions yields a crystalline *tetra-acetyl* derivative, $C_{19}H_{12}O_{10}(OAc)_4$, m. p. 176° , although the substance contains six hydroxyl groups. After previous drying in a vacuum over sulphuric acid, this acetyl derivative loses $1H_2O$ at 80° in a vacuum over phosphorus pentoxide, apparently from a non-acetylated grouping, $C \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$. The author



proposes for mangiferin (= euxanthogen) the annexed constitution. The transformation to euxanthic acid would take place by addition of a molecule of water at the ester grouping, rotation

of the ring on the left through 180° , and elimination of water to form the γ -pyrone ring.

G. B.

Additive Compounds of Gold Haloids with Benzyl Sulphide. GEORGE MCPHAIL SMITH (*J. Amer. Chem. Soc.*, 1922, 44, 1769-1775).—The two compounds which are produced by the interaction of gold chloride with benzyl sulphide (Hermann, A., 1905, i, 733) are additive compounds of gold monochloride and gold dichloride, respectively, with benzyl sulphide. They are conjugated compounds, probably constituted as shown in the formulae, $[ClAu \dots S(CH_2Ph)_2]$ and $[Cl_2Au \dots S(CH_2Ph)_2]$.

Unlike the additive compounds with platinum chloride, $[ClPt \begin{smallmatrix} \text{SR}_2 \\ \text{SR}_2 \end{smallmatrix}]$, which unite with further molecules of the organic sulphides to form interpolation compounds, such as $[Pt, 4SR_2]Cl_2$ (cf. Tschugaev and Benevolenski, A., 1913, i, 1149; Tschugaev and Kobljanski, A., 1913, i, 1149; Tschugaev and Chlopin, A., 1914, i, 479), the conjugate compounds of gold mono- and di-

chlorides appear to be incapable of yielding interpolation compounds by the further addition of benzyl sulphide. Dichloro-gold-benzyl sulphide probably exists in chloroform solution as a solvate of the formula $\text{Cl}_2\text{AuS}(\text{CH}_2\text{Ph})_2\cdot\text{CHCl}_3$.

The compound $\text{Br}_2\text{AuS}(\text{CH}_2\text{Ph})_2$, prismatic needles of a dark maroon colour, is prepared by extracting an aqueous solution of chloroauric and constant-boiling hydrobromic acids with ether and addition of benzyl sulphide to the ethereal extract. It is transformed when heated with alcohol into the compound $\text{BrAuS}(\text{CH}_2\text{Ph})_2$, long, colourless, transparent needles. The substance $\text{I}_2\text{AuS}(\text{CH}_2\text{Ph})_2$, black, prismatic needles, is prepared similarly to the corresponding dibromo-compound; attempts to isolate the compound $\text{IAuS}(\text{CH}_2\text{Ph})_2$ were not successful. The substance $\text{CHAuS}(\text{CH}_2\text{Ph})_2$ is also described. H. W.

Preparation of Symmetrical Aryl Alkyl Ethers. FARREN. FARRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 343930; from *Chem. Zentr.*, 1922, ii, 700).—Aryl alkyl haloids are heated with alkali hydroxides. *Dibenzyl ether* is prepared by heating benzyl chloride with potassium hydroxide at 180 – 200° or with sodium hydroxide at 90 – 120° . It is a colourless liquid with slight blue fluorescence, b. p. 285 – 290° . *Ditolyl dimethyl ether* has b. p. 300 – 310° . The products have uses as solvents. G. W. R.

The Solubility of the Alkali Salts of Benzoic and the Hydroxybenzoic Acids in Water. NEVIL VINCENT SIDGWICK and ELINOR KATHARINE EWBANK (T., 1922, 121, 1844–1853).

The Reaction of Organomagnesium Compounds on Nitriles. Action of Magnesium Methyl Bromide on Phenylacetonitrile. ALB. RONDOU (*Bull. Soc. chim. Belg.*, 1922, 31, 231–241).—Magnesium methyl bromide acts in an analogous manner to metallic sodium on the nitrile, producing new substances from it by polymerisation. Two of these have been obtained pure and examined. The chief product is a bimolecular polymeride, previously obtained by von Meyer (A., 1895, i, 582) as an oil, but now as crystals of m. p. 114.5 – 115° . It is stated that crystallisation is hindered by traces of impurities. The ternolecular polymeride differs from those previously prepared, and an attempt to investigate its structure leads to the conclusion that it is 4 : 6-diamino-3 : 5-diphenyl-2-benzylpyridine (cf. Wedekind, A., 1911, i, 219). H. J. E.

The Action of Acetic Anhydride on some Benzylidene-anthranilic Acids. V. J. B. EKELEY, E. C. ROGERS, and MARGARET SWISHER (*J. Amer. Chem. Soc.*, 1922, 44, 1756–1758).—In previous papers (A., 1912, i, 211; 1913, i, 395; 1914, i, 576; 1915, i, 166), it has been shown that oxazine derivatives are produced when acetic anhydride reacts with benzylideneanthranilic acids. The reaction has been extended further to a large number of aldehydes and appears to be of very general applicability. The acids are usually very readily prepared but, for some unexplained reason, the condensation of anthranilic acid with cuminal or β -naphthaldehyde methyl ether could not be effected. Un-

expectedly, *o*-nitropiperonal gives two anthranilic acid derivatives which are convertible into different oxazines, thus indicating the possibility that *o*-nitropiperonal is in reality a mixture of two very similar nitration products.

The following benzylidenanthranilic acids are obtained by mixing molecular proportions of the requisite aldehyde and anthranilic acid in concentrated alcoholic or benzene solution at 0°. 3-Nitrosacylideneanthranilic acid, orange-red needles, m. p. 227°. 5-Nitrosacylideneanthranilic acid, orange-red needles, m. p. 270°. 2:4-Dinitrobenzylidenanthranilic acid, mustard-coloured prisms, m. p. 153°. *m*-Tolylidenanthranilic acid, orange-red crystals, m. p. 202.5°. *p*-Diethylaminobenzylidenanthranilic acid, red needles, m. p. 154°. Terephthalylidenanthranilic acid, yellow crystals, m. p. 300°. *p*-Ethoxybenzylidenanthranilic acid, yellow needles, m. p. 117°. *o*-Methoxybenzylidenanthranilic acid, yellow needles, m. p. 130°. β -Hydroxynaphthylidenanthranilic acid, orange crystals, m. p. 252°. 4-Methoxy-3-methylbenzylidenanthranilic acid, straw-coloured needles, m. p. 161°. 3:4-Dimethoxybenzylidenanthranilic acid, pale yellow needles, m. p. 169°. *o*-Carboxybenzylidenanthranilic acid, colourless crystals, m. p. 225°. Nitropiperonylidenanthranilic acid (α -form), yellowish-brown crystals, m. p. 185° (decomp.). Nitropiperonylidenanthranilic acid (β -form), yellow crystals, m. p. 128°. 2:4:5-Trimethoxybenzylidenanthranilic acid, orange-yellow crystals, m. p. 151°. *p*-Homosalicylideneanthranilic acid, red needles, m. p. 209°.

These acids yield the oxazine derivatives either by heating molecular proportions with acetic anhydride in xylene solution for several hours under a reflux condenser or by heating them with an excess of acetic anhydride and removing the excess by distillation. With terephthalylidenanthranilic acid, the reaction is effected in boiling nitrobenzene. The following individual substances are described: 4-Acetyl-3-3'-nitro-2'-acetoxyphe-nyldihydro-

2:4-benzoxazine-1-one, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}=\text{O} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{Ac} \quad \text{CH} \cdot \text{C}_6\text{H}_3(\text{OAc})\text{NO}_2 \end{smallmatrix}$, colourless crystals, m. p. 190°. 4-Acetyl-3-5'-nitro-2'-acetoxyphe-nyldihydro-2:4-benzoxazine-1-one, colourless crystals, m. p. 178°. 4-Acetyl-3-2':4'-dinitrophenyldihydro-2:4-benzoxazine-1-one, straw-coloured crystals, m. p. 110°. 4-Acetyl-3-2'-acetox-4'-methoxyphenyldihydro-2:4-benzoxazine-1-one, colourless crystals, m. p. 156°. 4-Acetyl-3-*p*-diethylaminophenyldihydro-2:4-benzoxazine-1-one, colourless crystals, m. p. 170°. 4-Acetyl-3-*p*-phenylenebisdihydro-2:4-benzoxazine-1-one, colourless crystals, m. p. 267°. 4-Acetyl-3-*p*-ethoxyphenyldihydro-2:4-benzoxazine-1-one, colourless crystals, m. p. 182°. 4-Acetyl-3-*o*-methoxyphenyldihydro-2:4-benzoxazine-1-one, colourless crystals, m. p. 178°. 4-Acetyl-3- β -acetoxynaphthyldihydro-2:4-benzoxazine-1-one, colourless crystals, m. p. 198°. 4-Acetyl-3-*p*-methoxy-*m*-tolylidihydro-2:4-benzoxazine-1-one, colourless crystals, m. p. 128°. 4-Acetyl-3-*mp*-dimethoxyphenyldihydro-2:4-benzoxazine-1-one, colourless crystals, m. p. 183°. 4-Acetyl-3-*o*-carboxyphenyldihydro-2:4-benzoxazine-1-one, colourless crystals, m. p. 134°. 4-Acetyl-3-nitro-3':4'-methylenedioxyphenyldihydro-2:4-benzoxazine-

1-one (α -form), brownish-yellow crystals, m. p. 206°. 4-Acetyl-3-nitro-3':4'-methylenedioxyphenyldihydro-2:4-benzoxazine-1-one (β -form), colourless crystals, m. p. 165°. 4-Acetyl-2:4:5-trimethoxyphenyldihydro-2:4-benzoxazine-1-one, colourless crystals, m. p. 135°. 4-Acetyl-3-o-acetoxy-p-tolyldihydro-2:4-benzoxazine-1-one, colourless crystals, m. p. 166°. H. W.

Researches on Residual Affinity and Co-ordination. X. Salicylatotetramminocobaltic Salts and the Constitution of Oxonium Compounds. GILBERT T. MORGAN and J. D. MATY SMITH (T., 1922, 121, 1956—1971).

New Synthesis of isoFerulic Acid [3-Hydroxy-4-methoxycinnamic Acid]. F. MAUTNER (J. pr. Chem., 1922, [ii], 104, 132—136).—3-Nitro-4-methoxycinnamic acid was prepared according to the instructions of Einhorn and Grabfield (A., 1888, 477), and found to melt at 248—249°, not 140°, as given by these authors. On reduction with ferrous sulphate and ammonia it yields 3-amino-4-methoxycinnamic acid, light, yellow crystals, m. p. 179—180°, which forms a diazo-compound, from which on boiling with dilute copper sulphate solution isoferulic acid, m. p. 228°, is obtained.

isoVanillin, prepared from protoatechualdehyde by partial methylation, condenses with malonic acid in presence of acetic acid, and at the same time carbon dioxide is eliminated and isoferulic acid formed. W. O. K.

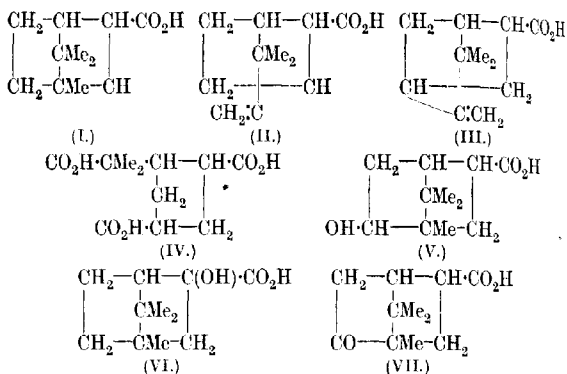
Formation and Properties of Fluorescein. O. FISCHER and MARTIN BOLLMANN (J. pr. Chem., 1922, [ii], 104, 123—131).—In fluorescein as ordinarily prepared there is at most only traces of resorcinolphthalein, a fact no doubt due to the instability of this compound at the temperature of the reaction. In presence of boric acid, however, the more stable boric acid ester is formed, and fair yields of resorcinolphthalein, nearly colourless crystals, m. p. 208—209°, are obtained (monoacetyl derivative, colourless needles, m. p. 161°). This forms a hydrochloride, $C_{20}H_{12}O_5.HCl$, reddish-yellow leaflets, on passing hydrogen chloride into its ethereal solution, or on boiling with concentrated hydrochloric acid and then adding alcohol. This compound is useful in separating the fluorescein formed from the resorcinolphthalein. The hydrobromide, small leaflets, and hydriodide, stellar aggregates of dark red needles, are formed in like manner. Fluorescein forms two mono- and two di-methyl ethers, one of each being coloured and one of each colourless. These yield the following salts: coloured monomethyl ether: hydrochloride, prisms, m. p. 212° (decomp.); hydrobromide; colourless monomethyl ether: hydrochloride, dark yellow leaflets, decomp. 170—173°, hydrobromide, yellow needles, in tufts; coloured dimethyl ether: hydrochloride, yellowish-red tufts of needles, decomp. 114°; hydrobromide, orange-red leaflets in bunches, decomp. 172°; colourless dimethyl ether: hydrochloride, dark coloured needles losing their colour at 140°; hydrobromide, orange leaflets, decomp. 92°, sulphate, reddish-yellow, microscopic prisms, m. p. 212°. W. O. K.

Camphene-*epi-sec.*-carboxylic Acids [1:1-Dimethyl-6-methylene-(1:2:2)dicycloheptane-3-carboxylic Acid], their Preparation from Bornylene-*epi*-carboxylic Acid, and their Transformation into *sec.*- β -Hydroxycamphane-*epi*-carboxylic Acid [2-Hydroxy-3-methyl-*meso*-dimethyl-(1:2:2)dicycloheptanecarboxylic Acid] and δ -Hydroxycamphane-*epi*-carboxylic Acid [4-Hydroxy-3-methyl-*meso*-dimethyl-(1:2:2)dicycloheptanecarboxylic Acid] (*o*- and *p*-Borneolcarboxylic Acids). J. BREDT (*J. pr. Chem.*, 1922, [ii], 104, 1-27; cf. Bredt and Sandkuhl, A., 1909, i, 498).—It has been previously suggested (*loc. cit.*) that by intermolecular change, two camphene-carboxylic acids, (II) and (III), should be obtained from bornylene-carboxylic acid (I). The acid (II) has already been obtained as its isomeric lactone, and (III) is now prepared for the first time.

The tertiary hydrobromide of camphene-*epi-sec.*-carboxylic acid, m. p. 157° (previously known as α -hydrobromobornylencarboxylic acid), is obtained by acting on bornylencarboxylic acid with fuming aqueous hydrogen bromide, and this on treatment with alkali readily yields the tertiary hydroxy-acid, m. p. 176° (*loc. cit.*). This acid on dry distillation under reduced pressure, or on steam distillation, yields an acid, m. p. 76–77°. The same acid may be obtained directly from the hydrobromide by distilling in steam, or better, by warming with quinoline. This acid proves to be *camphene-epi-sec.-carboxylic acid*, b. p. 156–157°/13–14 mm., 132–133°/4 mm., 114°/1 mm. It crystallises from acetone or alcohol in plates. Treatment with hydrogen bromide yields the hydrobromide, m. p. 157°, from which the hydroxy-acid, m. p. 176°, and camphene-carboxylic acid, m. p. 76–77°, can again be obtained. With hydrogen bromide dissolved in acetic acid likewise, camphene-carboxylic acid hydrobromide is formed and no isomerisation to bornylencarboxylic acid takes place. It forms a silver salt, $C_{11}H_{15}O_2Ag$, small leaflets, not hygroscopic, an *ethyl* ester, b. p. 121–126°/15 mm., 128–130°/22 mm., $[z]_D^{20} +4.04^\circ$, n_D^{20} 1.47604. On treatment with mercuric acetate, a white precipitate soon separates, $C_{13}H_{20}O_5Hg$, indicating a terminal $\dot{C}=\text{CH}_2$ group (Balbiano's reaction). It is oxidised by permanganate to *carboxycamphenecamphoric acid* (IV), nodular crystals, m. p. 234–236°. The *anhydride* of camphene-carboxylic acid is formed on treating the hydroxy-acid, m. p. 176°, with boiling acetic anhydride. It is a liquid, $C_{22}H_{30}O_3$, b. p. 260–270°/13–15 mm.

Camphenecarboxylic acid on treatment with acetic acid and a few drops of sulphuric acid yields a product which is separated by fractional distillation into a higher and a lower boiling fraction. From the lower boiling fraction has been separated *p*-borneol-carboxylolactone (*d*+*l*)-bornylene carboxylic acid, and an unsaturated acid apparently isomeric with bornylencarboxylic acid. The higher boiling fraction consists of *acetyl- δ -hydroxycamphane-epi-carboxylic acid* (*acetyl borneol-p-carboxylic acid*), water-clear, prismatic crystals, m. p. 159°; on hydrolysis with potassium hydroxide solution, the above-mentioned *borneol-p-carboxylic acid* (V), leaflets, m. p. 180–181°, is obtained, and α -(*d*+*l*)-*sec.*- β -endo-

acetoxycamphane-epi-carboxylic acid [(*d*+*l*)-*acetylisoborneol-o-carboxylic acid*], hard, glistening prisms, m. p. 116°, yielding (*d*+*l*)-*isoborneol-o-carboxylic acid* (VI), small leaflets, m. p. 172°, on hydrolysis. With permanganate, borneol-*p*-carboxylic acid is oxidised to *δ*-ketocamphane-*epi-carboxylic acid* (*p*-camphocarboxylic acid) (VII), tufted needles, m. p. 133—134°, whereas (*d*+*l*)-*isoborneol-o-carboxylic acid* is unchanged, but is oxidised by nitric acid to camphoric acid. It is converted by acetic anhydride into (*d*+*l*)-bornylene *epi-carboxylic acid*, m. p. 110—111°, which is also formed on dry distillation of (*d*+*l*)-*acetylisoborneol-o-carboxylic acid*.



W. O. K.

Tropinonecarboxylic Acid Esters. R. WILLSTÄTTER, O. WOLFES, and H. MAEDER (U.S. Pat. 1419091).—Succindialdehyde is condensed with the mono-calcium salt of ethyl aceto-dicarboxylate and methylamine. The tropinone *ester* formed is an oily substance which hardens when exposed to air and takes up 2 mols. of water; m. p. 62—63° (*picrate*, m. p. 133—135°).

CHEMICAL ABSTRACTS.

Tropinonecarboxylic Acid Esters. O. WOLFES and H. MAEDER (U.S. Pat. 1419092).—An aqueous solution of succindialdehyde is added to a solution of an acetoacetic ester, alkali, and methylamine and the reaction product shaken with chloroform; the chloroform solution thus obtained is extracted with dilute sulphuric acid to obtain (on adding soda and extracting with chloroform) a tropinonecarboxylic acid ethyl ester, an oily substance which solidifies on exposure to the air for some time.

CHEMICAL ABSTRACTS.

Reduction of Acid Chlorides to Aldehydes by Means of Nickel Catalysts. H. SCHLIEWIENSKY (*Z. angew. Chem.*, 1922, 35, 483).—The preparation of aldehydes from acid chlorides by means of hydrogen in the presence of Kelber's nickel catalyst (A., 1917, ii, 215), has been described by Rosenmund (A., 1918,

i, 300). The author's attempts to repeat the preparation of benzaldehyde according to these directions have been unsuccessful. The reaction could not be effected in the presence of catalysts prepared from freshly precipitated basic nickel carbonate which was (a) ignited, while moist in air to the oxide and subsequently reduced by hydrogen in an electric furnace at 310—320°, (b) directly heated in the tube at 310—320° and subsequently reduced at the same temperature, and (c) dried at 100° in air and then ignited and reduced in hydrogen at 310—320°. Failure cannot be attributed to inactivity of the catalyst which rapidly caused the hydrogenation of fats.
H. W.

Reduction of Acid Chlorides to Aldehydes by Means of Nickel Catalysts. K. W. ROSENMUND (*Z. angew. Chem.*, 1922, 35, 483).—In reply to Schlievinsky (preceding abstract), it is pointed out that attention has already been directed (A., 1918, i, 300) to the variability in the behaviour of palladium and nickel as catalysts in the conversion of acid chlorides into aldehydes by hydrogen. A trustworthy procedure has been given in the case of palladium (Rosenmund and Zetsche, A., 1921, ii, 320); a modified method will be published in the case of nickel. H. W.

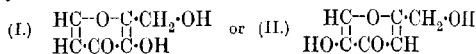
N-Oximino-ethers. II. N-Aryl Ethers of 2:4- and 2:6-Dinitrobenzaloximes. FRED BARROW, EVAN DALTON GRIFFITHS, and EDWARD BLOOM (T., 1922, 121, 1713—1717).

The Action of Sodium Methoxide and its Homologues on Benzophenone Chloride and Benzylidene Chloride. III. JOHN EDWIN MACKENZIE (T., 1922, 121, 1695—1699).

Piperitone. IV. The Interaction of *dl*-Piperitone and Semicarbazide, and the Isolation of Pure *dl*-Piperitone. JOHN READ and HENRY GEORGE SMITH (T., 1922, 121, 1863—1872).

A New Organic Acid (Kojic Acid) Formed by *Aspergillus oryzae*. TELIRO YABUTA (*J. Chem. Soc. Tokyo*, 1916, 37, 1185—1233, 1234—1269).—The substance is not only present in the organism, but is also formed abundantly when the latter is grown on steamed rice ("Koji") or in a 10% solution of dextrose with salts; in the latter case, one-tenth of the dextrose is converted according to the equation $C_6H_{12}O_6 + O = C_6H_8O_4 + 3H_2O$. The formula originally given (A., 1913, i, 180) must be halved, as the result of molecular weight determinations. Kojic acid thus differs by one oxygen atom from maltol, which is formed from carbohydrates on distillation (A., 1910, i, 719). Both substances are 3-hydroxy- γ -pyrones and give with ferric chloride a coloration similar to that given by salicylic acid; kojic acid gives this reaction even at 1:200,000. The acid forms colourless, anhydrous needles, m. p. 132°, subliming in a high vacuum without change, readily soluble in water, alcohol, or ethyl acetate, less soluble in ether, chloroform, or pyridine, scarcely at all soluble in most other solvents. The acid is precipitated by carbon dioxide from concentrated solutions of its sodium salt. It gives a red coloration

with *p*-diazobenzenesulphonic acid, and reduces Fehling's and ammoniacal silver solutions. The *copper* salt, $(C_6H_5O_4)_2Cu$, is the most characteristic of several crystalline salts, and is employed in the isolation of the substance. The *barium* salt has the composition $(C_6H_5O_4)_2Ba \cdot 2C_6H_5O_4$; the *calcium* and *strontium* salts have a similar composition, $+4H_2O$. The *diacetyl* derivative, $C_6H_4O_2(OAc)_2$, m. p. 102° , the *dibenzoyl* derivative, m. p. 136° , the *diphenylcarbamate*, $C_6H_4O_2(O \cdot CO \cdot NHPh)_2$, m. p. 170° , and the *monobenzoyl* derivative, $C_6H_5O_3(OBz)$, m. p. 135° , have been prepared, the latter by benzoyl chloride acting on the substance suspended in ether. The *dimethyl ether*, $C_6H_4O_2(OMe)_2$, prepared by diazomethane or methyl sulphate, m. p. 90° , is hydrolysed by boiling barium hydroxide solution into equimolecular proportions of formic acid, methoxyacetic acid, and methoxyacetone (acetyl-carbinyl methyl ether). Ammonia transforms kojic acid into a *base*, $C_8H_{11}O_5N$, probably the dimethyl ether of a hydroxy-methyl-hydroxy- γ -pyridone (comenamic alcohol?). This base was isolated as the *hydrochloride*, m. p. $180-181^\circ$, the *picrate*, m. p. 177° , and the *platinichloride*, m. p. 172° . The above facts suggest that kojic acid has either of the following constitutions:



In the case of maltol, Peratoner and Tamburello (A., 1905, i, 807) decided between similar alternatives in favour of a formula analogous to I, and Peratoner and Palazzo (A., 1905, i, 806) assigned to comenic acid a constitution of the second type, because the latter does, and maltol does not, react with benzenediazonium acetate or amyl nitrite (only compounds of the second type can tautomerically furnish the $\cdot CH_2 \cdot CO \cdot$ grouping necessary for these condensations). Since kojic acid forms with benzenediazonium acetate a *benzenediazo-derivative*, $C_{12}H_{10}O_4N_2 \cdot H_2O$, m. p. (in sealed tube) $146-147^\circ$, the author considers that it is constituted according to formula II, so that it would be 3-hydroxy-6-hydroxy-methyl- γ -pyrone, the alcohol corresponding with comenic acid. Various unsuccessful attempts at the conversion of kojic acid into known pyrone and pyridone compounds were made by oxidation and reduction.

Bromine water yields *monobromokojic acid*, $C_6H_5O_4Br$, m. p. $159-160^\circ$, furnishing a *copper* salt, $(C_6H_4O_4Br)_2Cu$, and with lead acetate and nitrate *double salts* of the compositions

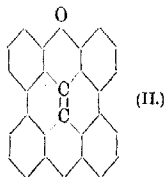
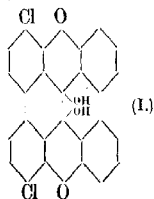
$C_6H_5O_4Br \cdot Pb \cdot C_6H_5O_4$
and $C_6H_5O_4Br \cdot Pb \cdot NO_3$. It yields a *diacetyl* derivative,

$C_6H_4O_2Br(OAc)_2$, m. p. $94-95^\circ$, and a *dibenzoyl* derivative, $C_6H_4O_2Br(OBz)_2$, m. p. $133-134^\circ$. It is converted by barium hydroxide in poor yield into *hydroxykojic acid*, $C_6H_6O_5 \cdot \frac{1}{2}H_2O$, which gives with ferric chloride a transitory green or, in the presence of sodium acetate, a purple coloration. Hydroxykojic acid is probably 2:3-dihydroxy-6-hydroxymethyl- γ -pyrone and yields an amorphous *copper* salt, $C_6H_4O_5Cu$. When the lead double salt of bromokojic and acetic

acid (above) is treated with hydrogen sulphide, a *sulphide*, $(C_6H_5O)_2S$, m. p. 210–212°, results. (Cf. also, for maltol, A., 1894, i, 270; 1895, i, 80, and for isomaltol, A., 1910, i, 544; further, Brill, A., 1916, i, 876.) G. B.

Highly Condensed Derivatives of Xanthone. ALFRED ECKERT and GERTRUD ENDLER (*J. pr. Chem.*, 1922, [ii], 104, 91–101).—Corresponding with anthraquinone, a *mesonaphthobianthrone* is known (Scholl, A., 1910, i, 494). The analogous *mesonaphthodixanthylene* is now described.

2:5-Dichlorophenol and *o*-chlorobenzoic acid are condensed by boiling methyl alcoholic potash in presence of copper powder to form *o*:2:5-dichlorophenoxybenzoic acid, a white, crystalline powder, m. p. 120–124°. Sulphuric acid converts this compound into 1:4-dichloroxanthone, long, colourless needles, m. p. 159–161°, which, when boiled with methyl alcoholic potash under a reflux condenser yields 4-chloro-1-methoxyxanthone, yellow needles, m. p. 156–158°. Aluminium chloride removes the methyl group from this, with the formation of 4-chloro-1-hydroxyxanthone, long, yellow needles, m. p. 156°. By treating 1:4-dichloroxanthone with copper powder in boiling naphthalene, 4:4'-dichloro-1:1'-dixanthonyl, long, colourless needles, m. p. 290°, is obtained, and this compound, on reduction with zinc dust in alcoholic potash, yields a *pinacone*, with the formula (I), yellow crystals, m. p. 276–278°. This substance can be very easily oxidised back to dichlorodixanthonyl with chromic acid. On further reduction with red phosphorus and hydrogen iodide, it yields *mesobenzdixanthylene*, golden-yellow plates, m. p. 236–237°. This substance on oxidation with chromic acid yields dixanthonyl, and when heated at 140–150° with aluminium chloride loses two atoms of hydrogen to form *mesonaphthodixanthylene*, yellow needles, m. p. 140–150° (II). It has not been found possible to carry out this last change, by illuminating a solution of *mesobenzdixanthylene* in acetic acid.



W. O. K.

Preparation of Benzanthrone Derivatives. BRITISH DYE-STUFFS CORPORATION, LIMITED, ARTHUR GEORGE PERKIN, and GEORGE DOUGLAS SPENCER (Brit. Pat. 183351).—*Hydroxybenzanthrone* is obtained by heating a mixture of benzanthrone (50 parts), anthraquinone (50 parts), alkali hydroxide (300 parts), water (75 parts), and sodium chlorate or sodium nitrate (35 parts) VOL CXXII. i.

in an autoclave slowly at 250° and then maintaining the temperature during three hours between 250° and 265°. The product is digested with boiling water, and anthraquinone removed by filtration. Hydroxybenzanthrone is precipitated from the filtrate by carbonic acid or a stronger acid.

Aminobenzanthrone is prepared by gradually heating a mixture of hydroxybenzanthrone (25 parts) and ammonia (*d* 0.880, 500 parts) in an autoclave at 200° and subsequently maintaining the temperature at 220–230° during seven hours. The product is diluted with water and filtered, whereby aminobenzanthrone is isolated as dull red crystals; unchanged hydroxybenzanthrone can be recovered by acidification of the filtrate. H. W.

Introduction of Arylamino-groups into Aminoanthraquinones. BADISCHE ANILIN & SODA-FABRIK (Fr. Pat. 526686; Brit. Pat. 171292; Swiss Pat. 90480; from *Chem. Zentr.*, 1922, ii, 639).—Aminoanthraquinones or their substituted derivatives are treated with metallic compounds of primary aromatic amines, or with such metals or metallic compounds, especially metallic amides, which give with amines metallic arylamine compounds, in the presence of weak oxidising agents such as air. For example, by heating 1-amino-2-methylantraquinone with sodium amide, or with sodium, magnesium, or aluminium anilides, 1-amino-4-anilino-2-methylantraquinone is obtained. 1-Amino-2-methylantraquinone and sodium *p*-toluidide similarly give 1-amino-4-*p*-toluidino-2-methylantraquinone, lustrous, metallic, dark violet prisms, m. p. 266°. Other compounds similarly prepared are the following. *s*-1:4-Dianilinoanthraquinone, lustrous, metallic, violet needles, m. p. 217°; *s*-1:4-Di-*p*-toluidinoanthraquinone; 1-amino-2-anilinoanthraquinone (?), violet, lustrous needles, m. p. 239°; 1-amino-4-anilinoanthraquinone, m. p. 192°; amino-*p*-toluidinoanthraquinone, m. p. 253°; amino-*o*-toluidinoanthraquinone, m. p. 206°; *s*-dianilinoanthraquinone, violet needles with slight metallic lustre, m. p. 152°; anthraquinonedihydro-5-phenylphenazine, m. p. 233° (cf. A., 1921, i, 274); diaminophenylaminoanthraquinone, dark violet crystals. G. W. R.

Preparation of 1-Amino-2-anthraquinone Aldehyde. LEOPOLD CASSELLA & Co., (D.R.-P. 346188 and Swiss Pat. 73683; from *Chem. Zentr.*, 1922, ii, 638).—The condensation products obtained by heating 1-amino-2-methylantraquinone with aromatic nitro-compounds, with or without addition of primary aromatic amines in the presence of alkalis, are treated with acids. The condensation product of the composition $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_2(NH_2)^1 \cdot (CH:N-Aryl)^2$ obtained by the action of 1-amino-2-methylantraquinone on nitrobenzene in the presence of potassium carbonate or on β -naphthylamine in the presence of nitrobenzene, is heated with sulphuric acid or with acetic acid and strong hydrochloric acid. The 1-aminoanthraquinone-2-aldehyde thus obtained, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_2(NH_2) \cdot CHO$, forms lustrous,

metallic, red crystals, m. p. 231—233°. The solution in strong sulphuric acid gives a diazo-compound with sodium nitrite. When heated with primary amines, it gives an azomethine. G. W. R.

Picolinoylaminoanthraquinones. E. DE BARRY BARNETT (*Chem. News*, 1922, **125**, 143—144).—1-Picolinoylaminoanthraquinone, $C_{20}H_{12}O_3N_2$, a dark yellow, crystalline powder, m. p. 282—284° (decomp.), is prepared by the action of crude picolinoyl chloride on a solution of 1-aminoanthraquinone in tetrachloroethane. On alkaline reduction, it forms a red vat-dye, but the action takes place slowly and with considerable difficulty. 2-Picolinoylaminoanthraquinone forms almost colourless crystals, m. p. 257—258°. The compounds could not be caused to react with alkyl haloid with the formation of soluble, quaternary (pyridinium) salts. H. W.

Anthraquinone Derivatives. K. WILKE (U.S. Pat. 1417875).—By the action of fuming sulphuric acid on 1-nitro-2-alkylantraquinones, products are formed which are insoluble in alkalis and are good starting materials for the manufacture of dyes. Conducting the reaction with exclusion of air gives products of greater purity. Elimination of the elements of water occurs between the nitro- and alkyl-group with formation of new isooxazole derivatives of anthraquinone. 1-Nitro-2-methylantraquinone yields 1:2-anthraquinoneisooxazole, m. p. about 250° (decomp.). 1:5-Dinitro-2-methylantraquinone yields greenish-yellow crystals of 5-nitro-1:2-anthraquinoneisooxazole. 1-Nitro-2-ethylantraquinone yields 1:2-anthraquinonemethylisooxazole, coarse, dark brown crystals, m. p. about 210°. 1-Nitro-2-methyl-5:6:7:8-tetrachloroanthraquinone yields 5:6:7:8-tetrachloro-1:2-anthraquinoneisooxazole, a greenish-yellow powder, m. p. about 242° (decomp.).
CHEMICAL ABSTRACTS.

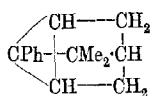
Preparation of Camphene Hydrochloride. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 348484; from *Chem. Zentr.*, 1922, ii, 699—700).—Camphene is treated, in the presence of a suitable diluent, with hydrogen chloride at low temperatures. The hydrochloride (formula annexed) thus obtained forms branched snow-white crystals, m. p. 125—127°. It has a strong odour similar to that of menthol, but quite distinct from that of pinene hydrochloride and isobornyl chloride. It is unstable and readily loses hydrogen chloride, which results in the gradual formation of isobornyl chloride. This transformation takes place more quickly in the presence of acids. By shaking camphene hydrochloride with water, camphene hydrate is formed in quantitative yield. The reaction takes place more quickly in the presence of alkalis. G. W. R.

The Borneol obtained from the Magnesium Compound of Pinene Hydrochloride. G. VAVON and A. L. BERTON (*Compt. rend.*, 1922, **175**, 369—372).—Pinene hydrochloride when treated with

Grignard's reagent and then oxidised yields a mixture of borneol and isoborneol in different proportions depending on the temperature of oxidation. The authors state that their experiments yield no evidence as to the stage at which the formation of two isomerides takes place and suggest the possibility of the existence of isomerides in the pinene hydrochloride.

H. J. E.

Phenylcamphenol. A. M. NORDSTRÖM (*Hyllningskrift tillägnad Ossian Aschan*, 1920, 129—133).—Magnesium phenyl bromide and camphenol yield a viscid, oily substance, *phenylcamphenol*, b. p. 166—167°/15 mm., d_4^{20} 1.0620, n_D^{20} 1.55085, and a little diphenyl. Elimination of water yields a compound, probably of the annexed



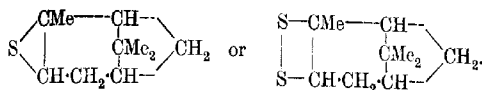
constitution, d_4^{20} 1.0002, n_D^{15} 1.54679. It does not form a nitrosochloride, but treatment with formic acid yields phenylapobornyl formate, a viscid oil, b. p. 183.5—185°/18 mm., d_4^{20} 1.0801, n_D^{20} 1.53461, by hydrolysis of the ester, of which there are obtained phenylapoborneol, b. p. 164.5—166°/7 mm., d_4^{20} 1.0583, n_D^{20} 1.55160, and an acid crystallising in fine needles, m. p. 164°. Phenylapoborneol on oxidation yields phenylapocamphor, b. p. 185—187°/20 mm., d_4^{20} 1.0716, n_D^{20} 1.55228 (semicarbazone, m. p. 214°); the latter on oxidation gives phenylapocamphoric acid, lustrous scales, m. p. 205° (anhydride, m. p. 118—119°; diethyl ester, b. p. 200—201°/7 mm., d_4^{20} 1.7028, n_D^{15} 1.50596). Phenylapoborneol yields, according to Chugaev, phenylapobornylene, b. p. 135°/13 mm., d_4^{20} 0.9907, n_D^{15} 1.54466 (nitrosochloride, m. p. 164°) and a substance, b. p. 70—74°/8 mm., d_4^{20} 0.9108, n_D^{17} 1.53619, which on oxidation gives benzyl alcohol and a ketone (semicarbazone, m. p. 196°).

CHEMICAL ABSTRACTS.

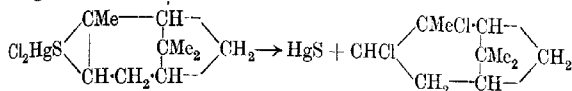
Action of Sulphur and Sulphur Compounds on Terpenes.

P. P. BUDNIKOV and E. A. SCHILOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk*, 1921, 4, 110—112).—When terpenes, b. p. 155—160°, are subjected to prolonged boiling with sulphur in a reflux apparatus and in an atmosphere of carbon dioxide, hydrogen sulphide and other gaseous products are formed together with a reddish-brown, oily liquid having a characteristic, acrid odour. Fractional distillation of this liquid at either ordinary or reduced pressure yields a number of products which all contain sulphur and form precipitates when treated with alcoholic solutions of mercuric chloride, auric chloride, and lead acetate. The mercury compound gradually decomposes with formation of mercuric sulphide and a red, oily liquid when boiled with water, and yields a distillate free from sulphur, but containing chlorine, when distilled in a current of steam. Hydrogen sulphide is also liberated when the fractions of the original product are treated with strong acids. Similar sulphur-containing products, giving precipitates with some of the heavy metal salts, are obtained when terpenes are treated with hydrogen sulphide under the conditions mentioned above.

Sulphur probably unites with terpenes at the double linking, giving a compound of the formula



In the compound formed with mercuric chloride, the latter probably unites with the sulphur, the subsequent decomposition by steam being represented by the equation :



T. H. P.

The Composition of Beechnut Oil (*Oleum fagi sylvaticæ*).

A. HEIDUSCHKA and P. ROSER (*J. pr. Chem.*, 1922, [ii], **104**, 137—160).—An exhaustive analysis shows the presence in this oil of 0.39% of α -linolenic acid, 9.19% of α -linolic acid, 76.69% of oleic acid, 4.88% of palmitic acid, 3.45% of stearic acid, and 0.82% of material which could not be saponified and was essentially phytosterol.

W. O. K.

The Essential Oil from Inchi Grass (*Cymbopogon Cæsius*, Stapf.). K. L. MOUTGILL and K. R. KRISHNA IYER (*Perf. and Essent. Oil Rec.*, 1922, **13**, 292—295).—The constants for this oil (yield, 0.8%) are: d_4^{20} 0.9187; n_D^{20} 1.484; $[\alpha]_D^{20}$ -38.9° ; acid number, 1.7; saponification number, 5.6; acetyl number, 120; percentage of aldehydes (Bennett's hydroxylamine method), 4.2. The oil is not identical with any of the known commercial oils from allied grasses, and may be used as a substitute for palmarosa oil, which it resembles in odour. It contains *l*-borneol, *l*-camphene, *l*-limonene, *l*-terpineol, and unidentified sesquiterpene constituents.

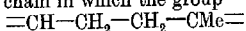
H. C. R.

Essential Oil of Juniper from Cyrenaica. V. MASSERA (*Riv. Ital. ess. profumi*, 1922, **4**, 23—24; from *Chem. Zentr.*, 1922, i, 1079).—A sample of essential oil of juniper from Cyrenaica had d_{25}^{25} 0.8715; $[\alpha]_D^{25}$ $+6^\circ$; n_D^{25} 1.4732; acid number, 0.54; esterification number, 4.91; acetyl number, 11.92. α -Pinene and cadinene were present. A sample from another locality had similar properties.

G. W. R.

Empirical and Structural Composition of Natural and Synthetic Caoutchouc. F. KIRCHHOFF (*Koll. Chem. Beihefte*, 1922, **16**, 47—87).—A critical discussion in which the author by means of an examination of the analytical data of Harries and his co-workers attempts to show that Para caoutchouc has the empirical formula $\text{C}_{10}\text{H}_{17}$. The African Congo caoutchouc has, like the synthetic isoprene and piperylene caoutchouc, the formula $\text{C}_{10}\text{H}_{16}$, which has been generally accepted for all forms of caoutchouc. These formulæ are in keeping with the behaviour of these substances during ozonisation and oxozonisation. Because of this new formula for Para caoutchouc, it must have a 'constitution different from

that put forward by Harries. The Para caoutchouc hydrocarbon must have an open chain in which the group



must appear, but in which other groups must also exist, as shown by the appearance of formic, carbonic, and succinic acids during the decomposition of the ozonide. Here, in part, is the difference between Para caoutchouc and synthetic isoprene caoutchouc. An attempt is made to build up structural formulae which shall represent the quantitative relationships of the ozonide decomposition, the depolymerisation in solution and the decomposition on distillation in a vacuum. Since the purely chemical structural formula is insufficient to represent both the chemical and physico-chemical facts, the author has advanced a special formula which, it is claimed, explains the colloidal, physico-chemical, and chemical properties of caoutchouc.

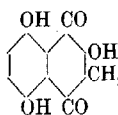
J. F. S.

Anemonins. YASUHIKO ASAHINA and ATSUSHI FUJITA (*Acta Phytchim.*, 1922, 1, 1—42).—A résumé in German of Asahina's work on anemonin, most of which has been published in Japanese only (cf. A., 1892, i, 241; 1896, i, 623; 1899, i, 930; 1914, i, 561; 1915, i, 1067; 1916, i, 401; 1920, i, 70, 321, 493, 678; 1921, i, 798).

W. G.

The Colouring Matter of *Lithospermum erythrorhizon*.

RIKŌ MAJIMA and CHIKA KURODA (*Acta Phytchim.*, 1922, 1, 43—65).—The colouring matter of shikon, the dried roots of *Lithospermum erythrorhizon*, has been isolated in a crystalline form and been shown to be a *monoacetyl* derivative, m. p. 85—86°, of shikonin. If the acetyl derivative is dissolved in dilute alkali and the solution is then acidified with dilute acid, shikonin itself, $C_{16}H_{16}O_5$, m. p. 147°, is obtained. It gives *sodium* and *copper* salts and on acetylation yields a *triacetyl* derivative, m. p. 113°, but if the acetylation is carried out in the presence of zinc dust, a *penta-acetyl* derivative of reduced shikonin, m. p. 90°, is formed, which on bromination gives a *bromo-compound*, $C_{16}H_{12}O_5BrAc_5 \cdot H_2O$, m. p. 123°. Shikonin also yields a *dibenzoyl* derivative, m. p. 168°, and an *oxime*, m. p. 163°. The constitution assigned to shikonin (annexed formula) is that of δ -methyl- Δ -



pentenyl-2:5:8-trihydroxy-1:4-naphthoquinone. In support of this view, it is shown that on heating, shikonin is partly converted into shikazarin (1:4-dihydroxy-8-methylanthraquinone), m. p. 232°, and on dry distillation gives 1- and 2-

methylanthracenes. Shikazarin, if distilled with zinc dust, gives the same products. When oxidised with potassium permanganate in acetone solution, shikazarin gives 3-methylphthalic acid. Triacetylshikonin on oxidation with ozone yielded acetone, succinic acid, and 3:6-dihydroxyphthalic acid.

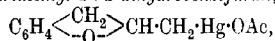
W. G.

The Structure of the Compounds produced from Olefines and Mercury Salts: Mercurated Dihydrobenzofurans. ROGER ADAMS, F. L. ROMAN, and W. N. SPERRY (*J. Amer. Chem. Soc.*, 1922, 44, 1781—1792).—Experimental evidence is adduced

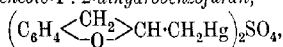
from the literature to disprove molecular formulæ, such as $\text{CH}_2\text{:CH}_2\text{Hg(OH)X}$, for the compounds from olefines and mercuric salts.

A series of mercurated dihydrobenzofurans of the general structure $\text{C}_6\text{H}_4\langle\text{CH}_2\text{O}\rangle\text{CH}\cdot\text{CH}_2\cdot\text{HgX}$, is described. These compounds are remarkably stable towards acids in comparison with other mercury salt-olefine compounds. They are converted by potassium iodide into the corresponding iodide and by treatment with sodium amalgam give compounds of the general type R_2Hg . No reasonable molecular formula for the mercurated dihydrobenzofurans can be written which will explain the structure and the chemical reactions of these compounds. The additive formula allows of a simple explanation of all the experimental facts.

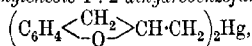
1-Acetoxymercurimethyl-1 : 2-dihydrobenzofuran,



colourless plates, m. p. $80-81^\circ$, is prepared by the gradual addition of an aqueous solution of mercuric acetate to a suspension of *o*-allylphenol in water. It is converted by sodium chloride solution into 1-chloromercurimethyl-1 : 2-dihydrobenzofuran, m. p. 137° , which is also obtained from *o*-allylphenol and mercuric chloride in the presence of water, ethyl alcohol, or *n*-butyl alcohol. If the reaction is effected in the presence of aqueous hydrochloric acid, an unstable intermediate compound, probably $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{HgCl}$, is also formed which, however, could not be isolated in a homogeneous condition. The acetoxy-compound is converted by hot potassium bromide solution into 1-bromomercurimethyl-1 : 2-dihydrobenzofuran, colourless, lustrous crystals, m. p. 122° , and by potassium iodide into 1-iodomercurimethyl-1 : 2-dihydrobenzofuran, colourless plates, m. p. $114-115.5^\circ$; the latter substance is also obtained from the chloromercuri-derivative and potassium iodide. 1:1-Sulphato-mercuridimethylenebis-1 : 2-dihydrobenzofuran,



m. p. 123° (decomp.), is prepared by the cautious addition of *o*-allylphenol to a solution of mercuric oxide in aqueous sulphuric acid. Reduction of 1-chloromercurimethyl-1 : 2-dihydrobenzofuran by sodium amalgam and ethyl alcohol leads to the production of 1:1-mercuridimethylenebis-1 : 2-dihydrobenzofuran,



colourless crystals, m. p. 93° .

o-Allylanisole reacts with an aqueous or methyl alcoholic solution of mercuric acetate with the formation of α -acetoxymercuri- γ -*o*-anisylpropan- β -ol, $\text{C}_6\text{H}_4(\text{OMe})\cdot\text{CH}_2\cdot\text{CH(OH)}\cdot\text{CH}_2\cdot\text{Hg}\cdot\text{OAc}$, which could not be caused to crystallise. It is readily decomposed by hydrochloric acid with regeneration of *o*-allylanisole. It appears to be converted by sodium chloride into the corresponding chloride, which could not be caused to solidify. Mercuric chloride or sulphate does not react with *o*-allylanisole.

1-Iodomercurimethyl-1:2-dihydrobenzofuran is transformed by a hot solution of iodine in aqueous potassium iodide into 1-iodo-

methyl-1:2-dihydrobenzofuran, $C_8H_4 \begin{smallmatrix} \text{CH}_2 \\ \diagup \text{O} \diagdown \end{smallmatrix} \text{CH} \cdot \text{CH}_2\text{I}$, colourless crystals, m. p. 36.5—37.5°, b. p. 150—151°/13—15 mm., d_{25}^{25} 1.792 (liquid), n_D^{25} 1.614; the latter substance is reduced by granulated zinc and hydrochloric acid to 1-methyl-1:2-dihydrobenzofuran, b. p. 199—202°/744 mm., d_{25}^{25} 1.507, n_D^{25} 1.536. H. W.

The Relation between Vitali's Reaction and the Constitution of the Alkaloids which give it. PAUL HARDY (*J. Pharm. Chim.*, 1922, [vii], 26, 172—176).—It has been pointed out that Vitali's reaction is given by substances other than atropine and hyoscyamine. The author shows that it is a general reaction for esters of certain acids the constitution of which is analogous to that of tropic acid. The reaction is given by scopolamine and by *iso*-atropylcocaine but not by homatropine or veratrine. H. J. E.

Salts of Codeine: The Hydrobromide; Preparation of Solutions for Injection. FELIX MARTIN (*J. Pharm. Chim.*, 1922, [vii], 26, 176—187).—Codeine hydrobromide crystallises with 2 mols. of water, which are not lost on exposure to the atmosphere; in dry air, $\frac{1}{2}$ mol. of water is lost at the ordinary temperature. At 100°, the salt is only partly dehydrated and must be heated at 115—116° before becoming anhydrous. The solubility in water at 97° is 2.04. Addition of sodium benzoate or salicylate increases its solubility at the ordinary temperature; this is considered to be due to double decomposition, as codeine salicylate may be extracted with ether from a mixed solution. Several analyses of commercial codeine indicate a product of a high degree of purity. H. J. E.

Harmine and Harmaline. VI. The Synthesis of N-Methyl-tetrahydronorharmine and the Constitution of Harmaline and of the Alkylated Harmines. WILLIAM OGILVY KERMACK, WILLIAM HENRY PERKIN, and ROBERT ROBINSON (*T.*, 1922, 121, 1872—1896).

Preparation of O-Alkyl Derivatives of Hydrocupreine. VEREINIGTE CHININFABRIKEN ZIMMER & Co., (D.R.P. 344140; from *Chem. Zentr.*, 1922, ii, 812).—Hydrocupreine oxide, which may be obtained by oxidation of hydrocupreine, is alkylated by the usual methods and the products are reduced to the alkyl derivatives of hydrocupreine. Since the nitrogen atom which is alkylated is protected by an oxygen atom, ammonium bases are not formed. *Hydrocupreine oxide* (leaflets, m. p. 199°, obtained by the action of 30% hydrogen peroxide on hydrocupreine) is treated with ethyl sulphate, *ethyl hydrocupreine oxide sulphate*, thereby obtained, forms colourless needles. By heating with excess of sulphur dioxide under pressure, *ethyl hydrocupreine* is obtained. By treatment of hydrocupreine oxide with ethylene chloride and

reduction with sulphuric acid and sodium sulphite, *chloroethyl hydrocupreine* is obtained; it forms colourless needles, m. p. 164° .
G. W. R.

The Isolation of Muscarine, the Potent Principle of *Amanita Muscaria*. HAROLD KING (T., 1922, 121, 1743—1753).

Arylated Pyridines and their Relations to the Corresponding Pyrylium Compounds. IV. WALTHER DILTHEY [with J. NÜSSLEIN, HEINR. MEYER, and H. KAFFER] (*J. pr. Chem.*, 1922, [ii], 104, 28—36; cf. A., 1921, i, 735).—It has been shown that whereas the salt-forming powers of pyrylium compounds are not much affected by the introduction of aryl groups, those of pyridine compounds are considerably weakened. It has now been found, however, that, under suitable conditions, penta- and tetraphenylpyridines form a picrate, and that pentaphenylpyridine forms a perchlorate, the basicity thus being rather stronger than had been suspected.

The following new compounds have been prepared: *Penta-phenylpyridine picrate*, nodular, yellowish-orange crystals or compact prisms, m. p. $233\text{--}237^{\circ}$, *perchlorate*, colourless crystals, m. p. 299° ; 2:4:5:6-tetraphenylpyridine *picrate*, small, yellow needles, m. p. $192\text{--}193^{\circ}$; 4:5:6-triphenyl-2-(p-bromophenyl)pyridine, colourless needles, m. p. 172° (*picrate*, m. p. 226°); 4-phenyl-2:6-di-(p-bromophenyl)pyridine, colourless, silky needles, m. p. 196° (*hydrochloride*, citron-yellow needles, *picrate*, yellow prisms, m. p. 212°); 4:6-diphenyl-2-(4-methoxy-3-methylphenyl)pyridine, colourless needles, m. p. 112° (*hydrochloride*, greenish-yellow crystals like glass-wool, m. p. $100\text{--}104^{\circ}$); 4:6-diphenyl-2-(6-hydroxy-m-tolyl)pyridine, colourless needles, m. p. $151\text{--}152^{\circ}$ (*picrate*, yellow needles, m. p. 232°); 4:6-diphenyl-2-(6-acetoxy-m-tolyl)pyridine, colourless prisms, m. p. $99\text{--}101^{\circ}$ (*picrate*, nodular, yellow crystals, m. p. $126\text{--}127^{\circ}$).

W. O. K.

Preparation of Hydrogenated 1-Alkylpyridine-4-Carboxylates. E. MERCK (D.R.-P. 344028; from *Chem. Zentr.*, 1922, ii, 810).—Trigonelline (methylbetaine of pyridine-3-carboxylic acid), its 1-alkyl homologues, or the salts of these compounds are reduced by metals in alcoholic solution. Reduction of trigonelline chloride by tin and hydrochloric acid in methyl alcoholic solution gives methyl 1-methylhexahydropyridine-3-carboxylate, an oil, b. p. $92\text{--}94^{\circ}/16$ mm. The alkylhaloids have therapeutic uses. The methiodide has m. p. 190° (corr.). Ethyl 1-ethylhexahydropyridine-3-carboxylate, a basic-smelling, colourless oil, b. p. $108\text{--}110^{\circ}/13$ mm., is obtained by reduction of ethyltrigonelline hydrochloride (? *hydrobromide*). The latter is prepared by heating pyridine-3-carboxylic acid with ethyl bromide, sodium carbonate, and water in a closed vessel; it forms white, lustrous spangles, m. p. 227° (decomp.).
G. W. R.

Preparation of Hydrogenated 1-Alkylpyridine-3-carboxylates. RICHARD WOLFFENSTEIN (D.R.-P. 346888; from *Chem. Zentr.*, 1922, ii, 811).—In the place of 1-alkylhaloids of alkyl pyridine-

3-carboxylates (this vol., i, 365), other quaternary ammonium salts are used. For example, methyl 1-methylpyridine-3-carboxylate methosulphate is reduced by tin and hydrogen chloride to methyl 1-methylhexahydropyridine-3-carboxylate, which is identical with the compound obtained by reduction of the corresponding 1-alkyl haloids. *Ethyl 1-ethylhexahydropyridine-3-carboxylate*, similarly prepared, is a basic, oily liquid. G. W. R.

Preparation of Alkyl Salts of Hydrogenated 1-Alkylpyridine-3-carboxylates. RICHARD WOLFFENSTEIN (D.R.P. 346461 and 348379; from *Chem. Zentr.*, 1922, ii, 810—811; cf. this vol., i, 365).—Hydrogenated 1-alkylpyridine-3-carboxylates are treated with alkyl haloids or with other alkyl salts. By the action of methyl iodide on methyl 1-methylhexahydropyridine-3-carboxylate in the presence of a diluent, the corresponding 1-methiodide is obtained. It is a colourless or light yellow, crystalline powder of fish-like odour, having m. p. 185—188°. The 1-methobromide is a white, crystalline powder, m. p. 196°. The 1-methochloride is prepared by the action of silver chloride on the 1-methiodide. The *ethosulphate* forms white, lustrous leaflets, m. p. 90—96°. The *ethosulphate* of ethyl 1-methylhexahydropyridine-3-carboxylate is also mentioned. The products have therapeutic uses. G. W. R.

Preparation of 1-Alkylpyridine Carboxylates. E. MERCK (D.R.-P. 344029; from *Chem. Zentr.*, 1922, ii, 810).—Betaines of the pyridine series are esterified with alcohols by the usual methods in the presence of strong acids. The *chloride of methyl 1-methylpyridine-3-carboxylate*, $C_8H_{10}O_2NCl \cdot H_2O$, is prepared by heating trigonelline or trigonelline chloride with methyl alcohol containing hydrochloric acid. It forms colourless crystals, m. p. 101°. G. W. R.

Preparation of Betaines of the Pyridine Series. E. MERCK (D.R.-P. 344030; from *Chem. Zentr.*, 1922, ii, 810).—Pyridine-carboxylic acids are treated with methyl chloride in alkaline solution at about 100°. Trigonelline is thus prepared from pyridine-3-carboxylic acid. Pyridine-2:3-dicarboxylic acid (quinolinic acid) gives a *methyl pyridine-2:3-dicarboxylic acid* having m. p. 157°. G. W. R.

The 6-Alkyloxy-2-methylquinolines. GURNEY O. GUTEKUNST and H. LE B. GRAY (*J. Amer. Chem. Soc.*, 1922, 44, 1741—1746).—The preparation of 6-alkyloxy-2-methylquinolines involves the production of relatively large quantities of the various *p*-amino-phenyl alkyl ethers, some of which are more conveniently obtained by the reduction of the corresponding *p*-nitrophenyl compounds, whereas others are derived more readily from the *p*-acetylaminophenyl alkyl ethers. The amines are transformed into the 2-methylquinolines according to the Doebner-Miller quinaldine synthesis.

p-Nitrophenyl butyl ether, slender, colourless needles, m. p. 32°, is prepared by the protracted heating of a solution of *p*-nitrophenol

in aqueous alcoholic (50%) potassium hydroxide solution with butyl alcohol and butyl iodide under a reflux condenser. *p-Aminophenyl butyl ether*, obtained by reducing the nitro-compound with stannous chloride and concentrated hydrochloric acid, is a pale yellow liquid, b. p. 143—144°/12 mm. *p-Nitrophenyl isoamyl ether*, a pale yellow liquid, b. p. 183°/18 mm., is reduced similarly to *p-aminophenyl isoamyl ether*, a pale yellow liquid, b. p. 149—150°/15 mm.

p-Acetylaminophenyl allyl ether, minute crystals, m. p. 88—89°, is prepared by the action of allyl bromide on a boiling solution of *p-acetylaminophenol* and potassium hydroxide in alcohol (75%). It is hydrolysed by sulphuric acid to *p-aminophenyl allyl ether*, a pale yellow liquid, b. p. 143—144°/13 mm., the *sulphate* of which, large, colourless plates, m. p. 244° (decomp.), is described. The following compounds have also been prepared: *p-Acetylaminophenyl butyl ether*, colourless needles, m. p. 112°; *p-aminophenyl butyl ether*, a pale yellow liquid, b. p. 143—144°/12 mm. [*sulphate*, large colourless plates, m. p. 270° (decomp.)]; *p-acetylaminophenyl benzyl ether*, colourless needles, m. p. 142°; *p-acetylaminophenyl isobutyl ether*, colourless needles, m. p. 80—81°; *p-aminophenyl isobutyl ether*, a colourless liquid, b. p. 145—146°/10 mm. [*sulphate*, large colourless plates, decomp. 251—252°]; *p-acetylaminophenyl isoamyl ether*, colourless plates, m. p. 103—103·5°; *p-aminophenyl isoamyl ether*, a pale yellow liquid, b. p. 149—150°/15 mm. [*sulphate*, colourless plates, m. p. 253—254° (decomp.)].

6-Propoxy-2-methylquinoline, a pale yellow liquid, b. p. 176—177°/16 mm., is prepared by the action of concentrated hydrochloric acid on a mixture of paracetaldehyde and *p-aminophenyl propyl ether hydrochloride*; the corresponding *ethiodide* crystallises in pale yellow needles, m. p. 147·5°. The following compounds are obtained in an analogous manner: *6-Allyloxy-2-methylquinoline*, a red, oily liquid, and the corresponding *ethiodide*, small, yellow needles which could not be purified satisfactorily; *6-butoxy-2-methylquinoline*, yellow nodules, m. p. 52° after softening at 48°, b. p. 182—183°/13 mm. (*ethiodide*, small, yellow needles, m. p. 186°); *6-isobutoxy-2-methylquinoline*, a colourless, oily liquid, b. p. 171—172°/12 mm. (*ethiodide*, small, yellow needles, m. p. 142°); *6-isoamylloxy-2-methylquinoline*, a pale yellow liquid, b. p. 182—183°/10 mm. (*ethiodide*, yellow needles, m. p. 201°). H. W.

Quinolines. I. Preparation of 6-Ethoxy-2:4-dimethylquinoline. S. PALKIN and M. HARRIS (*J. Ind. Eng. Chem.*, 1922, 14, 704—705).—The method employed is a modification of that described by Mikeska, Haller, and Adams (*A.*, 1921, i, 54). The reaction product is distilled in steam for half an hour, cooled, decanted, and the tarry residue washed with dilute hydrochloric acid, which is added to the main liquid. Excess of sodium hydroxide solution is added and the oil which slowly rises to the surface is removed and distilled under reduced pressure (30—70 mm.). The oil is collected up to 225°/30 mm. The crude base is treated on a steam-bath with acetic anhydride and poured into water. Most

of the primary base and the hydro-base are thus removed as insoluble acetyl compounds. The filtrate is treated with excess of sodium hydroxide solution, and the solidified base removed, dissolved in twice its weight of hydrochloric acid, and diazotised.

On dilution with water, the hydrochloride of the base dissolves, leaving a residue containing phenacetin and the nitroso-compound. The filtrate is steamed for twenty minutes to decompose diazonium salts, filtered through cotton, and neutralised. The base solidifies and is collected on a filter and distilled in a vacuum. It is then recrystallised from 18% hydrochloric acid and the solution filtered in three stages—namely, at 40–50°, at room temperature, and at 0°. The product has b. p. 314–316° and m. p. 88–88.5°. Boiling range curves for the crude base and after the diazotisation process are given.

A. G. P.

Preparation of Substituted Derivatives of Hydrogenated 2-Phenylquinoline-4-carboxylic Acid, and their Salts. FRITZ ZUCKMAYER (D.R.-P. 344501; from *Chem. Zentr.*, 1922, ii, 811).—

An earlier patent (this vol., i, 574) is modified, whereby in place of 2-phenylquinoline-4-carboxylic acid, hydroxy-, amino-, or acetyl-amino-derivatives substituted in the quinoline group are used. By reduction of 7-acetylamino-2-phenylquinoline-4-carboxylic acid with sodium amalgam, 7-acetylamino-2-phenyltetrahydroquinoline-4-carboxylic acid is obtained; it forms yellowish-brown crystals, m. p. 210°, and gives a light yellow nitroso-compound. The potassium salt is a tasteless, yellow powder. Reduction of 6-hydroxy-2-phenylquinoline-4-carboxylic acid (a yellow mass, m. p. above 300°) yields 6-hydroxy-2-phenyltetrahydroquinoline-4-carboxylic acid; it is a white, tasteless powder, m. p. 248–250° (decomp.). The tetrahydro-compounds may be acetylated, and form nitroso-compounds.

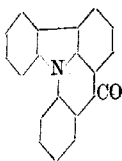
G. W. R.

Preparation of 2-ar-Tetrahydronaphthylquinoline-4-carboxylic Acids. CHEMISCHE FABRIK AUF AKTIEN (FORM. E. SCHERING) (D.R.-P. 344027; from *Chem. Zentr.*, 1922, ii, 811–812).—

Isatins are condensed with ar-acetyltetrahydronaphthalenes in alkaline solution. 2-ar-Tetrahydronaphthylquinoline-4-carboxylic acid, from the condensation of isatin with ar-acetyltetrahydronaphthalene, forms dark yellow, transparent leaflets, m. p. 196–197.5°. With 6-bromoisatin, 7-bromo-2-ar-tetrahydronaphthylquinoline-4-carboxylic acid is obtained; it forms yellow crystals, m. p. 228–229.5°.

G. W. R.

Phenylcarbazole. ALFRED ECKERT, FRITZ SEIDEL, and GERTRED ENDLER (*J. pr. Chem.*, 1922, [ii], 104, 85–90).—Carbazole, when heated in a reflux apparatus with o-iodobenzoic acid in nitrobenzene solution in the presence of potassium carbonate and copper oxide yields carbazole-o-benzoic acid, white, lustrous needles, m. p. 184° (methyl ester, long needles, m. p. 138–140°). This decomposes at 350–400° to yield 9-phenylcarbazole, m. p. 94–95°, purified as the picrate, m. p. 126–129°. When heated with



m. p. 158—160°.

zinc chloride at 280°, carbazole-9-benzoic acid yields an acridone derivative (annexed formula), crystals, m. p. 190°. This is also formed on boiling carbazole-9-benzoic acid in xylene solution with phosphorus pentachloride and then adding aluminium chloride. On reduction in alcoholic solution with sodium, the derivative yields the dihydroacridine derivative, $C_{19}H_{13}N$, yellow needles, W. O. K.

Preparation of an Unsaturated Ether of *p*-Dihydroxydiphenylacetamidine. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 91728; from *Chem. Zentr.*, 1922, ii, 699).—*p*-Aminophenyl allyl ether is condensed with *p*-acetylaminophenyl allyl ether in the presence of phosphorus compounds such as phosphorus haloids, phosphoric oxide, phosphoryl chloride, or phosphoryl bromide, using benzene or toluene as diluting agents. The diallyl ether of *p*-dihydroxyphenylacetamidine thus obtained forms colourless crystals, m. p. 85—86°. The hydrochloride is crystalline, m. p. 152—153°. This product has a more powerful local anæsthetic action than the corresponding saturated ethers.

G. W. R.

Glyoxalinedicarboxylic Acid for the Recognition and Separation of Organic Bases. H. PAULY and E. LUDWIG (*Z. physiol. Chem.*, 1922, 121, 165—169).—Glyoxalinedicarboxylic acid forms sparingly soluble and well crystallised mono-hydrogen salts with a number of organic bases. The hydrogen salts with the following bases have been prepared: Methylamine, m. p. 240—245°; dimethylamine, m. p. 238—239°; trimethylamine, m. p. 260—265°; ethylamine, m. p. 253—254°; diethylamine, m. p. 180°; propylamine, m. p. 212°; *n*-butylamine, m. p. 225—227°; piperidine, m. p. 221—222°; *d*-coniine, m. p. 208—209°; atropine, m. p. 93°; the solubility of these being between 2 and 45 per cent., but with those of hydrazine, m. p. above 260°; guanidine, m. p. 241—242°, glyoxaline, m. p. 245°, and *l*-histidine, m. p. 253—254° (decomp.), the solubilities are very small. The ionisation constants for the two stages of ionisation are $K_1=0.00285$ and $K_2=6.44 \times 10^{-8}$.

H. K.

Glucosamine as the Basis of Formation of Heterocyclic Compounds. HERM. PAULY and ERNST LUDWIG (*Z. physiol. Chem.*, 1922, 121, 170—176).—Glucosamine forms heterocyclic compounds of the glyoxaline and pyrrole type more easily than dextrose. By condensation with silver cyanate, *glucimidazolone* (5- α , β , δ -tetrahydroxybutylglyoxal-2-one), $C_7H_{12}O_5N_2 \cdot \frac{1}{2}H_2O$, is obtained, m. p. 130—135°, and $[\alpha]_D^{20}=-49.4^\circ$ in water, and from potassium thiocyanate in a similar manner, 2-thiolglucimidazole, $C_7H_{12}O_4N_2S \cdot H_2O$, m. p. 168°, and $[\alpha]_D^{20}=-17.9^\circ$ in water. On oxidation with hydrogen peroxide, the latter gives *glucinimidazole hydrochloride*, m. p. 162°, but when oxidised with dilute nitric acid an impure additive product of the silver salt and silver nitrate was

obtained. Stronger nitric acid gave glyoxalinecarboxylic acid. Glucosamine condenses at 100° with acetoacetic ester or acetyl acetone, giving, respectively, the ethyl ester of 2-methyl-5- $\alpha\beta\gamma\delta$ -tetrahydroxybutylpyrrole-3-carboxylic acid, m. p. 120° , and $[\alpha]_D + 49.7^\circ$ in water, and 3-acetyl-2-methyl-5- $\alpha\beta\gamma\delta$ -tetrahydroxybutylpyrrole, m. p. 98° , and $[\alpha]_D - 25.1^\circ$ in water. H. K.

Preparation of Aminoacetyl Compounds of 4-Amino-1-phenyl-2:3-dialkylpyrazolones. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Aust. Pat. 86136; from *Chem. Zentr.*, 1922, ii, 575).—Aqueous ammonia is allowed to act on 4-chloroacetyl-amino-1-phenyl-2:3-dialkylpyrazolones, or the additive compounds of the latter with hexamethylenetetramine are treated with acids. 4-Chloroacetyl-amino-1-phenyl-2:3-dimethyl-5-pyrazolone, m. p. 187° , is prepared by the action of chloroacetyl chloride on 4-amino-1-phenyl-2:3-dimethyl-5-pyrazolone. The additive compound with hexamethylenetetramine gives by treatment with strong hydrochloric acid 4-aminoacetyl-amino-1-phenyl-2:3-dimethyl-5-pyrazolone (formula annexed). It forms a dihydro-

chloride, m. p. about 233° , and a monohydrochloride, m. p. $260-265^\circ$. The aminoacetyl compound may also be prepared by the action of aqueous ammonia on the chloroacetyl compound. 4-Chloroacetyl-amino-1-phenyl-3-methyl-2-ethyl-5-pyrazolone (m. p. 186°) gives with aqueous ammonia 4-aminoacetyl-amino-1-phenyl-3-methyl-2-ethyl-5-pyrazolone. The hydrobromide has m. p. about 150° . The compounds have antipyretic properties. G. W. R.

Hydantoins. Synthesis of the Soporific 4-Phenyl-4-ethyl-hydantoin [Nirvanol]. WILLIAM T. READ (*J. Amer. Chem. Soc.*, 1922, 44, 1746—1755).—The synthesis is effected in accordance with the scheme: $\text{COEtPh} \xrightarrow{\text{HCN}} \text{CN}\cdot\text{CetPh}\cdot\text{OH} \xrightarrow{\text{NH}_3} \text{CN}\cdot\text{CetPh}\cdot\text{NH}_2$
 $\xrightarrow[\text{HCl}]{\text{KOCN}} \text{CN}\cdot\text{CetPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 \xrightarrow{\text{H}_2\text{O} + \text{HCl}} \text{CO} \begin{array}{l} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CetPh} \end{array}$

The preparation of propionyl chloride by the action of chlorine on a mixture of propionic acid and sulphur monochloride is described. The optimal conditions for obtaining phenyl ethyl ketone from benzene, propionyl chloride, and aluminium chloride have been ascertained. Phenyl ethyl ketone does not react with ammonium cyanide in aqueous or dilute alcoholic solution, whilst the yields are poor in 95% alcoholic solution. Reasonably good results are obtained when an absolute ethyl alcoholic solution of ammonium cyanide (made by the action of ammonia on hydrogen cyanide dissolved in alcohol) is employed. The best results are secured when dry ammonium cyanide dissolved in a small amount of ethyl alcohol is allowed to react with phenyl ethyl ketone or when a mixture of hydrogen cyanide and phenyl ethyl ketone dissolved in alcohol is treated with ammonia. Under the best conditions, the yield of phenylethylaminoacetonitrile is 90% of

that theoretically possible, allowance being made for the recovered phenyl ethyl ketone, since the conversion is never complete. The yield does not appear to be affected by an excess of the reagent or the volume of solvent. The reaction is carried out at atmospheric temperature, the time being from one to four days.

Phenylethylaminoacetonitrile reacts with potassium cyanate in glacial acetic acid to form the nitrile of phenylethylhydantoic acid in 80% yield. When this compound is boiled with hydrochloric acid (20%), it is converted into 4-phenyl-4-ethylhydantoin, the yield being 85%. It is possible to prepare the latter substance by the procedure outlined above from phenyl ethyl ketone without isolating and purifying the intermediate products; the yield is 62% of that theoretically possible.

Potassium or ammonium thiocyanate does not react with phenylethylaminoacetonitrile in glacial acetic acid solution; phenylethylacetylaminooacetic acid or its nitrile is not acted on by potassium thiocyanate in the presence of acetic anhydride.

Phenylethylaminoacetonitrile is transformed by acetic anhydride into *phenylethylacetylaminooacetonitrile*, $\text{NHAc}\cdot\text{C}\cdot\text{EtPh}\cdot\text{CN}$, m. p. 147°; *phenylethylacetylaminooacetic acid*, prepared by the action of dilute hydrochloric acid on the nitrile, has m. p. 225° (decomp.).

H. W.

The Preparation of 6:6'-Di- α -hydroxyisopropylindigotin from *p*-Cymene. MAX PHILLIPS (*J. Amer. Chem. Soc.*, 1922, 44, 1775—1780).—*p*-Cymene is obtained by the distillation of spruce turpentine (cf. Schorger, A., 1917, i, 467) with steam, agitation of the distillate with sodium hydroxide solution and water, desiccation over calcium chloride, digestion over sodium, and fractional distillation. It is converted into mononitrocymene by a modification of the method described by Andrews (A., 1918, i, 339). The nitro-compound is oxidised by potassium permanganate in the presence of sodium hydroxide to *o*-nitro-*p*- α -hydroxyisopropylbenzoic acid, colourless crystals, m. p. 168° (corr.), which is reduced by tin and hydrochloric acid, ferrous sulphate, and ammonia or (preferably) ferrous sulphate and barium hydroxide to *o*-amino-*p*- α -hydroxyisopropylbenzoic acid, colourless plates, m. p. 158° (corr.). The latter is transformed by chloroacetic acid into *o*-aminoacetic-*p*- α -hydroxyisopropylbenzoic acid, $\text{CMe}_2(\text{OH})\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, faintly yellow, probably triclinic, crystals, m. p. 232.6° (corr.). Fusion of the acid with potassium hydroxide at 180—230°, and subsequent oxidation of the aqueous solution of the melt by air, gives 6:6'-di- α -hydroxyisopropylindigotin, which closely resembles indigotin in appearance. It dyes cotton from a hyposulphite bath greenish-blue, and compares rather favourably with indigotin as regards fastness to light, acid, washing, and rubbing. It differs from indigotin notably in its solubility in most organic solvents.

H. W.

The Cyanine Dyes. V. The Virtual Tautomerism of the Thiocyanines. WILLIAM HOBSON MILLS and WALTER THEODORE KARL BRAUNHOLTZ (T., 1922, 121, 1489—1495).

Dyes Derived from Phenanthraquinone. I. Phenanthra-naphthazines. ANUKUL CHANDRA SIRCAR and SIKHIBHUSAN DUTT (T., 1922, **121**, 1944—1951).

Dyes Derived from Phenanthraquinone. II. Naphtha-flavindulines. SIKHIBHUSAN DUTT (T., 1922, **121**, 1951—1955).

Synthesis of Substantive Azo-dyes derived from Naphthalene. N. N. VOROSHOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk*, 1921, **4**, 95—109).—In so far as the formation of azo-colouring matters of substantive character is concerned, the analogues of benzidine in the naphthalene series are, not the bimolecular naphthidines, but the unimolecular naphthylenediamines with the two amino-groups in the 1:5-, 1:4-, 2:6-, and 1:6-positions. The scale of colours given by these colouring matters approximates to that obtained with the corresponding compounds of the benzidine series.

T. H. P.

Attempts to prepare Red Sulphide Dyes. I. EDWIN ROY WATSON and SIKHIBHUSAN DUTT (T., 1922, **121**, 1939—1943).

The Constitution of the Products Arising from the Condensation of o-Aminoazo-compounds with Aldehydes. I. OTTO FISCHER (*J. pr. Chem.*, 1922, [ii], **104**, 102—122).—The colourless bases obtained by Goldschmidt (A., 1890, 614; 1891, 839) by the action of aldehydes on o-aminoazo-compounds, and considered by him to be triazines, are now shown to be derivatives

of 1-aminobenziminazole, $C_6H_5 \begin{smallmatrix} & NH_2 \\ & \diagup \\ < N & \\ & \diagdown \\ & CH \end{smallmatrix}$, as they are converted by hydrogen iodide into a derivative of benziminazole, and an amine, and also as they can be synthesised from such a benziminazole derivative by heating the chloroimide, obtained from it on treatment with a hypochlorite, with a base. Moreover, it has in certain cases been found possible to isolate the Schiff's base compounds formed as intermediate stages in the condensation to Goldschmidt's bases, corresponding with the Schiff's base compounds obtained by the action of aldehydes on p-aminoazo-compounds.

[With WOLFGANG MEIER].—From p-tolueneazo-β-naphthylamine and salicylaldehyde in methyl alcohol in presence of piperidine, tolueneazo-o-hydroxybenzylidene-β-naphthylamine is formed, deep red prisms, m. p. 162°, and this compound, on longer boiling in alcohol, acetic acid, formic acid, or alcoholic hydrogen chloride, or on heating with pyridine, further condenses to 1-p-toluidino-2-o-hydroxyphenylnaphthiminazole, white, compact crystals, m. p. 192° (diacetyl compound, white, compact crystals, m. p. 180° [decomp.]). Similarly, p-tolueneazo-β-naphthylamine yields with furfuraldehyde p-tolueneazofurfurylidene-β-naphthylamine, needles, m. p. 66°, which further condenses to 1-p-toluidino-2-furylnaphthiminazole, white needles, m. p. 215° (nitrosoamine, light yellow, compact crystals, decomp. about 150—160°); and with benz-

aldehyde, 1-*p*-toluidino-2-phenyl- α -naphthiminazole, needles, m. p. 208° (*nitrosoamine*, light yellow crystals).

The following compounds have been similarly prepared from *o*-aminoazo-*p*-toluene. 1-*p*-Toluidino-2-phenyl-5-methylbenziminazole, m. p. 231° (*nitrosoamine*, compact, yellow crystals, m. p. 129°); 1-*p*-toluidino-2-*o*-hydroxyphenyl-5-methylbenziminazole, white needles, m. p. 197—198° (*diacetyl* derivative, microcrystalline structure, but not crystallisable), 1-*p*-toluidino-2-furyl-5-methylbenziminazole, white, compact crystals, m. p. 227°.

[With H. SCHWAPPACHER.]—The following compounds are obtained similarly. From benzeneazo- β -naphthylamine and paraformaldehyde, 1-anilino- α -naphthiminazole, colourless prisms, m. p. 184° (*hydrochloride*, white needles, m. p. 254°, *picrate*, yellow, pointed crystals, m. p. 206—207°; *nitrosoamine*, long yellow needles, m. p. 120—121°). From *o*-tolueneazo- β -naphthylamine, compact prismatic dark red crystals, m. p. 125—126° (*acetyl* compound, fine, light red needles, m. p. 150—151°), and paraformaldehyde, 1-*o*-toluidino- α -naphthiminazole, yellow, crystalline powder, m. p. 166—167° (*nitrosoamine*, m. p. 130° [decomp.]) is formed. From *o*-tolueneazo- β -naphthylamine, with acetaldehyde, 1-*o*-toluidino-2-methylnaphthiminazole, colourless prisms, m. p. 169—170° (*acetyl* compound, small prisms, m. p. 117—118°); with benzaldehyde, 1-*o*-toluidino-2-phenyl- α -naphthiminazole, colourless needles, m. p. 210—211° (*picrate*, pointed, yellow crystals, m. p. 181—182°); with salicylaldehyde, 1-*o*-toluidino-2-*o*-hydroxyphenylnaphthiminazole, fine needles, m. p. 194—195°; with *p*-hydroxybenzaldehyde, 1-*o*-toluidino-2-*p*-hydroxyphenylnaphthiminazole, colourless, granular crystals, m. p. 228° (*nitrosoamine*, yellow, crystalline powder, decomp. 100°; *diacetyl* compound, coarsely granular crystals, m. p. 208°); with furfuraldehyde, 1-*o*-toluidino-2-furylnaphthiminazole, fine, colourless needles, m. p. 194—195° (*nitrosoamine*, yellow crystals, m. p. 147° [decomp.]).

[With H. KRACKER.]—On treating naphthiminazole with a hypochlorite 1-chloro- α -naphthiminazole, colourless, flat prisms, m. p. 198—199°, is obtained. This reacts with *p*-toluidine to yield 1-*p*-toluidino- α -naphthiminazole, short needles, m. p. 221—222°, identical with the base obtained by Goldschmidt from formaldehyde and *p*-tolueneazo- β -naphthylamine. In the same way, hypochlorite yields with 2-methyliminazole, 1-chloro-2-methyl- α -naphthiminazole, fine needles, m. p. 229°, which reacts with aniline to give 1-anilino-2-methylnaphthiminazole, m. p. 231—232°, identical with the substance formed from acetaldehyde and benzeneazo- β -naphthylamine, and with toluidine, to give 1-toluidino-2-methylnaphthiminazole, m. p. 197—198°, obtained from *p*-tolueneazo- β -naphthylamine and acetaldehyde. W. O. K.

A New Fractionation Method for Proteins and their Derivatives. M. A. RAKUSIN (*Biochem. Z.*, 1923, 130, 432—441).—The filtrates from a 95% alcoholic extract of a large number of animal and vegetable proteins and of enzymes were tested qualitatively by various colour reactions and found to contain

carbohydrate and nitrogenous substances in most cases. Pepsin-fibrin peptone can be fractionated by extraction with 95% alcohol and subsequent successive treatment of the filtrates with a 10% suspension of aluminium hydroxide for periods of twenty-four hours each, into a number of fractions which differ from one another in their colour reactions to various protein and carbohydrate reagents.

H. K.

Combined Action of Enzymes. A. J. J. VANDEVELDE (*Natuurwetenschapp. Tijdschr.*, 1921, 3, 200—203).—The assumption that enzymic action in a living organism is due to the combined action of several enzymes is tested by experiment. The action of a mixture of invertase (extracted from yeast) and of amylase (extracted from malt) is compared with the action of each enzyme alone. No increased action could be observed although the experiment was repeated in various ways. There is no evidence of a difference in the action of enzymes alone and in mixtures.

CHEMICAL ABSTRACTS.

The Action of Chymosin and Pepsin. VII. Further Experiments on the Purification of the Enzyme of the Stomach. OLOF HAMMARSTEN (*Z. physiol. Chem.*, 1922, 121, 240—260).—The starting material was prepared by extraction of the mucous membrane of the pig's stomach with 0.2% hydrochloric acid and precipitation of the "crude pepsin" as a hyaline mass by half saturation with sodium chloride. Preliminary experiments are described in which the sodium chloride is dialysed away in 0.2% hydrochloric acid solution and the solution kept at 37—38° to denature. The solution was then either (1) dialysed against water, (2) precipitated by half saturation with sodium chloride, or (3) precipitated by saturation with ammonium sulphate. A detailed account is to follow later. The present communication deals with the fractional extraction of the "crude pepsin" by water in a centrifuge, dialysis of the extracts and analysis of their contents in organic matter, pepsin, and chymosin. The successive extracts except the later ones compare favourably in activity with Pekelharing's pepsin, although the qualitative reactions are different. A comparison of the clotting time on milk (chymosin factor) and the digestive action by Mett's test (pepsin factor) of the author's preparation with Pekelharing's preparation showed no parallelism under any conditions. The author's solutions are stable, very faintly acid, and lose activity rapidly if neutralised.

H. K.

The Action of Chymosin and Pepsin. VIII. Relative Sensitiveness to Alkali of the Stomach Enzymes of the Calf and Pig. OLOF HAMMARSTEN (*Z. physiol. Chem.*, 1922, 121, 261—282).—Michaelis and Rothstein (*A.*, 1920, i, 775) found that alkali destroyed chymosin and pepsin from the pig's stomach at the same rate, whilst the author (*A.*, 1915, i, 911) found that these enzymes when prepared from the calf's stomach were acted on by alkali at totally different rates. This is now ascribed to the influence of the use of different animals. Chymosin from the pig's

stomach is destroyed much more rapidly than from the calf's and the same probably applies to the pepsin. Moreover, the experiments show the distinct entities of chymosin and pepsin as they are destroyed at different rates.

H. K.

The Proteolytic Enzymes of Malt. HARRY LUNDIN (*Biochem. Z.*, 1922, **131**, 193—218).—The optimum P_H for malt peptase is 3·7—4·3 in malt, and 3·2 in green malt. Malt peptase is not found in malt germ. The malt tryptase of green malt and of malt germ acts best at P_H 6·3. At the optimum P_H neutral salts have little action. The autolytic process in malt is conditioned by the various enzymes, each having their own optimum P_H . For the autolysis, the general optimum P_H is 4·3—5·0 in malt, 4·4 in green malt, and 6·3 in malt germ.

H. K.

Inactivation of Saccharase by Small Quantities of Silver Salts. H. VON EULER and KARL MYRBÄCK (*Z. physiol. Chem.*, 1922, **121**, 177—182).—Euler and Svanberg (*ibid.*, 1919, **107**, 269, 302) had previously shown that whilst invertase was inhibited by silver salts in proportion to their concentration, mercuric salts behaved differently, the results lying on a curve. A re-examination of the effect with silver salts reveals, however, a parallelism with mercury salts, the previous results being due to the observation now recorded that the results depend greatly on the concentration of the enzyme.

H. K.

Toxicity. The Combined Action of Quinine and of Narcotics on Invertase and on the Action of Arsenic Compounds on Maltase, and on α -Methylglucosidase. P. RONA, Y. AIRILA, and A. LASNITZKI (*Biochem. Z.*, 1922, **130**, 582—591).—The combined inhibitory actions of quinine and narcotics on invertase is less than the sum of their individual actions. Arsenious acid, arsenic acid, and atoxyl had no action on maltase or on α -methylglucosidase, but methylarsenious oxide was inhibitory.

H. K.

Amylases of the Cereal Grains—The "Insoluble" Amylase of Barley. JULIAN LEVETT BAKER and HENRY FRANCIS EVERARD HULTON (*T.*, 1922, **121**, 1929—1934).

Emulsin. II. RICHARD WILLSTÄTTER and GERTRUD OPPENHEIMER (*Z. physiol. Chem.*, 1922, **121**, 183—194; cf. this vol., i, 282, 284, 390).—In continuation of previous work, it is found that those enzyme actions of the emulsin complex which proceed best in a decidedly acid medium follow the unimolecular law, as, for instance, the hydrolysis of salicin, arbutin, phenylglucoside, and helicin. By comparing the time at which 50% of the following glucosides have been hydrolysed, helicin, salicin, phenylglucoside, arbutin, methylglucoside, prunasin, and amygdalin, by nine totally distinct preparations of emulsin, it is found that the ratio of the time values for helicin, salicin, and phenylglucoside alone is the same in each case. This is the first quantitative demonstration that one enzyme of the emulsin complex can attack different substrates. This enzyme, phenylglucosidase, is most specific for helicin.

H. K.

The Enzyme Hydrolysis of Benzyl Succinate. J. W. HOWARD (*J. Amer. Chem. Soc.*, 1922, **44**, 1763—1765; cf. Shonle and Row, A., 1921, i, 341; Christman and Lewis, A., 1921, i, 755; Volwiler and Vliet, this vol., ii, 41).—The lipase of the pancreas hydrolyses dibenzyl succinate only to benzyl hydrogen succinate; the latter is not hydrolysed by this enzyme. H. W.

The Chemical Action of Rennin. G. S. INICHOV (*Biochem. Z.*, 1922, **131**, 97—108).—There is no appreciable increase of acidity on addition of rennin to milk or caseinogen solutions under various conditions. Peptonisation does not therefore occur. The action of rennin is purely physical, the formation of casein being due to a change in the degree of dispersity of the solution under the influence of the ferment and in presence of bivalent ions and hydrogen ions. H. K.

Phosphatases. I and II. M. TOMITA (*Biochem. Z.*, 1922, **131**, 161—169, 170—174).—I. Saccharophosphatase. Animal organs possess a phosphatase which can hydrolyse saccharose monophosphate. The order of activity of the organs is: kidney, liver, spleen, pancreas, brain, and, least of all, muscle. The enzyme is thermo-labile.

II. Hexosemonophosphatase. The kidneys, spleen, liver, and muscle of cold- and warm-blooded animals can hydrolyse hexose monophosphate. Muscle extract exerts the weakest action. The action is more pronounced in each case than with saccharo-phosphatase. H. K.

Comparative Study of Ring-substituted Phenylphosphinic and Phenylarsinic Acids. D. R. NISK (*Rec. trav. chim.*, 1922, **41**, 461—500).—A comparison of the aromatic derivatives of nitric, phosphoric, and arsenic acids shows that nitrobenzene, phenylphosphinic acid, and phenylarsinic acid are very stable compounds from which the acidic group is not easily removed. In the case of the two last-named, removal of the group may be effected by very energetic methods. However, on the introduction of an amino-group in the ortho- or para-position with respect to the acidic group, the stability of the resulting phosphinic or arsenic acid undergoes considerable modification, although no such change is observed in *o*-nitroaniline or *p*-nitroaniline, the nitro-group remaining quite stable. The author points out that *p*-aminophenylphosphinic acid is less stable than the corresponding arsenic compound. If the amino-group be introduced into the meta-position with respect to the acidic group, no such change of stability takes place; it is a matter of some difficulty to remove the acidic group from *m*-aminophenylphosphinic and *m*-aminophenylarsinic acids. The author considers that the compounds studied exhibit an alternation of properties in aromatic derivatives of the same type containing nitrogen, phosphorus, and arsenic.

Full experimental detail of the work is given, and methods of preparation are described for 3-nitrophenylphosphinic acid, 3-amino-

phenylphosphinic acid, *p*-aminophenylarsinic acid, 5-nitro-2-aminophenylarsinic acid, phenylarsinic acid, and 3-nitrophenylarsinic acid, which are claimed to be more satisfactory than those previously published. The nitration of phenylphosphinic acid was effected at 0°; it has been stated (Michaelis and Benzinger, A., 1878, 57) that a temperature of 110° is necessary. The method specified in the patent (D.R.-P. 264924) for the preparation of phenylarsinic acid is criticised.

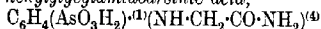
The following substances do not appear to have been previously described: 3-nitro-4-aminophenylphosphinic acid, deep yellow plates, m. p. 231° (decomp.); *m*-carbethoxyaminophenylphosphinic acid, thick, white plates, m. p. 140°, saponified on boiling in aqueous solution, cannot be diazotised, and gives no coloration with β -naphthol; nitro-3-carbethoxyaminophenylphosphinic acid, a bright yellow substance, explodes on heating; the aqueous solution does not react with nitrite, and is turned deep yellow by sodium hydroxide; 2-(?)nitro-3-aminophenylphosphinic acid, deep yellow needles, m. p. 185°.

H. J. E.

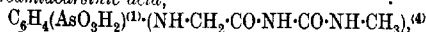
The Crystalline Form of Atoxyl [Sodium *p*-Aminophenylarsinate]. G. GILTA (*Bull. Soc. chim. Belg.*, 1922, 31, 211—213).—Detailed measurements of the crystals were made in order to obtain a rapid method of distinguishing between this substance and sodium diaminodiphenylarsinate. Monoclinic, $a:b:c = 2.481:1:0.963$, $\beta = 97^\circ 40'$. The work of Melon (*Bull. Acad. Roy. Belg.*, 1922, 50) is criticised.

H. J. E.

Preparation of Aromatic Aminoarsinic Acids. ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH (Dutch Pat. 6581; from *Chem. Zentr.*, 1922, ii, 873—874).— α -Halogenacylamides of the composition $X \cdot CHR \cdot CO \cdot NR_1R_2$ (where $X = \text{halogen}$, $R = \text{alkyl, aryl or hydrogen}$, $R_1, R_2 = \text{alkyl, aryl, substituted aryl, or hydrogen}$) are allowed to act on aminophenylarsinic acid, its homologues, its derivatives (substituted in the nucleus), or the salts of these compounds. *p*-Phenylglycylamidoarsinic acid,



is obtained by the action of chloro- or iodo-acetamide on the sodium salt of *p*-aminophenylarsinic acid; it forms colourless crystals, m. p. above 280°. The sodium salt forms colourless masses of crystals. By treating an alkaline solution of *p*-aminophenylarsinic acid with chloroacetylcarbamide, *p*-phenylglycylcarbamidoarsinic acid, $C_6H_4(AsO_3H_2)^{(1)}(NH \cdot CH_2 \cdot CO \cdot NH \cdot CO \cdot NH_2)^{(4)}$ is obtained. *p*-Phenylglycinearsinic acid is formed from this acid by hydrolysis; it has m. p. above 280°. The sodium salt contains two molecules of water of crystallisation. From α -chloroacetyl-methylcarbamide and *p*-aminophenylarsinic acid, *p*-phenylglycyl-methylcarbamidoarsinic acid,



is obtained; it forms colourless crystals, m. p. 232°. *p*-Phenylglycylanilinoarsinic acid, prepared similarly, using iodoacetanilide, forms a crystalline mass. *p*-Phenylglycyl-*m'*-aminophenylarsinic

acid is prepared by the action of 3*N*-chloroacetyl-amino-1-hydroxybenzene on *p*-aminophenylarsinic acid in alkaline solution. It forms small plates, m. p. above 230°.

G. W. R.

Preparation of Aromatic Arseno-compounds. ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH (Dutch Pat. 6352; from *Chem. Zentr.*, 1922, ii, 573—574).—Aminophenylarsinic acids or aminophenylarsenoxides, unsubstituted in the aromatic nucleus, in which a hydrogen atom of the amino-group is replaced by an acylarylamino-group of the composition $-\text{CHR}\cdot\text{CO}\cdot\text{NHR}_1$ (R=alkyl, aryl, or hydrogen; R₁=aryl with one or more acid groups such as hydroxyl, sulphonamide, carboxyl, or sulphonic acid) are reduced by ordinary methods to corresponding arseno-compounds. Phenylglycyl-*m'*-aminophenol-*p*-arsinic acid is reduced by hypophosphorous acid and hydriodic acid to the corresponding arseno-compound, which is a yellow powder, m. p. 180—190°. The dihydrochloride forms a light yellow powder, m. p. about 130°, which can only be kept in sealed vessels in the presence of indifferent gases, or in a vacuum. Phenylglycyl-*m'*-aminophenol-*p*-arsenoxide, $\text{AsO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, is prepared by reduction of the corresponding arsinic acid with sulphur dioxide and hydriodic acid. It is a white powder with m. p. above 200° after softening at 130°. Phenylglycylanthranilic acid-*p*-arsenoxide, $\text{AsO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, is similarly prepared. The compounds have therapeutic uses in trypanosome and spirochete infections.

G. W. R.

Physiological Chemistry.

Preparation of Crystalline Oxyhæmoglobin. MICHAEL HEIDELBERGER (*J. Biol. Chem.*, 1922, 53, 31—40).—The method described depends on the fact that the washed corpuscles from dog's or horse's blood crystallise almost completely in the presence of toluene when saturated with a mixture containing four parts of carbon dioxide to one part of oxygen. The oxyhæmoglobin so obtained may be recrystallised by dissolving in sodium carbonate solution and reprecipitating by saturation with the above mixture of gases. Salts may be removed from the recrystallised product by pressure dialysis. It is essential to perform all operations in the cold and in the presence of excess of carbon dioxide, and to prevent the oxyhæmoglobin becoming dry at any stage. Using this method, preparations with 96—100% of the theoretical oxygen capacity have been obtained.

E. S.

Effect of Carbon Dioxide on Sugar in Blood. FRIEDRICH BINSWANGER (*Pflüger's Archiv*, 1922, 193, 296—312; from *Chem. Zentr.*, 1922, i, 1053—1054).—Increase in the proportion of carbon dioxide in the air induces hyperglycæmia in rabbits, cats, and dogs.

Whilst increase in blood sugar is first observed in rabbits when 20% of carbon dioxide is present, 7% suffices to induce the condition in cats. The nature of the diet is without influence. Diminution of the pressure of carbon dioxide by forced respiration is without effect on the sugar content of the blood in man. Carbon dioxide hyperglycæmia is probably due to general cell injury, as it is accompanied by a marked fall in body temperature. G. W. R.

Adrenaline Hyperglycæmia. CH. ACHARD, A. RIBOT, and LÉON BINET (*Rev. méd.*, 1921, **38**, 447—456; *Ber. ges. Physiol.*, **11**, 319; from *Chem. Zentr.*, 1922, i, 987—988).—The percentage increase in blood-sugar and its duration depend on the amount of dextrose injected. With injection of dextrose and adrenaline, hyperglycæmia is more pronounced. Hypophysis extract exerts the same effect. With dextrose and aqueous pancreatic extract, the hyperglycæmia is less than with dextrose alone. Pancreatic extract partly neutralises the effect of adrenaline in adrenaline hyperglycæmia. G. W. R.

Partition of Urea in Blood. G. ETIENNE and M. VÉRAIN (*Compt. rend. soc. Biol.*, 1922, **86**, 394—395; from *Chem. Zentr.*, 1922, i, 1054).—Marked differences are found in the urea contents of blood and blood-clot. The amount of urea found in each component depends on the length of contact between clot and plasma. In experiments with liquids containing blood corpuscles, addition of trichloroacetic acid prevents diffusion of urea. G. W. R.

The Lipoids of the Blood in Tuberculosis. B. H. HENNING (*J. Biol. Chem.*, 1922, **53**, 167—170).—The blood of twenty-one tuberculosis patients was found to contain normal amounts of lecithin and of total fatty acid. When estimated without saponification, the content of cholesterol was also normal, but was uniformly low when the saponification method was employed. It is concluded that, in tuberculosis, the cholesterol of the blood is partly replaced by a related substance giving the same colour reaction. High values were obtained for "residual" fatty acid. E. S.

Biochemistry of Methyl Alcohol Poisoning. I. M. RABINOWITZ (*Arch. int. Med.*, 1922, **29**, 821—827).—In the case of a woman of seventy years, who lived for six days after taking methyl alcohol, the following results were observed: blood, increase of uric acid to 9.3 mg. per 100 c.c., urea to 144 mg., and creatinine to 4.5 mg., decrease in oxygen-saturation (15.5%); plasma, decrease in carbon dioxide (26%). On the last three days, the acid-soluble phosphorus content of the blood varied between 8.6 and 10.8 mg. per 100 c.c., and the dextrose content was 225 mg. per 100 c.c. The blood did not contain methæmoglobin. CHEMICAL ABSTRACTS.

Buffer Systems of Blood-serum. EDWARD A. DOISY, JULY P. EATON, and K. S. CHOUKE (*J. Biol. Chem.*, 1922, **53**, 1—74).—Experiments on the increased binding power of serum for carbon dioxide with increased tensions of this gas have been

extended (cf. A., 1921, i, 753). Buffers due to the presence of the corpuscles are termed "loaned" buffers, and those independent of the corpuscles (phosphates, serum-proteins) "self-possessed" buffers. Average results from a number of experiments on defibrinated human and dog's blood indicate that, between the P_H range of 7.45 and 7.25, 16% of the base furnished for the increase of hydrogen carbonate in serum comes from self-possessed non-migrating serum buffers, 1 to 3% of this being supplied by phosphates, whilst loaned buffers supply 84%. Of the latter, 80% is due to the migration of hydrochloric acid into the corpuscles, and the remainder probably to the similar migration of other acids.

E. S.

Total Nitrogen and Residual Nitrogen Content of Oedematous Fluids. RUDOLPH STRISOWER (*Wiener Arch. inn. Med.*, 1922, 4, 115—120).—Normal values of the content of residual nitrogen in oedematous fluids lie between 0.02 and 0.05%; the content is parallel to the total protein content. The value is usually higher than that of the blood, and is increased in cardiac insufficiency, arteriosclerosis of the kidney and chronic parenchymatous nephritis. There does not appear to be any direct relation between the uræmia and the increase of residual nitrogen in the oedematous fluid.

CHEMICAL ABSTRACTS.

Solubility, Capillary Activity, and Hæmolytic Activity of Terpene Derivatives. HEINRICH RHODE (*Biochem. Z.*, 1922, 130, 481—496).—The above-named properties of camphor, borneol, menthone, menthol, α - and β -terpineol, and norcamphor have been determined without revealing a relation between the physical properties and the hæmolytic values. The hæmolytic value of a substance is the same above or below its melting point. H. K.

Effect of Ether on Anti-substances. J. FORSSMAN (*Compt. rend. Soc. Biol.*, 1922, 86, 495—497; from *Chem. Zentr.*, 1922, i, 1055).—When heated with ethyl ether at 56°, hæmolysin is destroyed whilst agglutinin is unaffected. Protective anti-substances behave normally. With sera, varying results are obtained owing to the presence of protective colloids. To this may be attributed the fact that anti-substances precipitated by ammonium sulphate behave differently from those precipitated by acetic acid and distilled water. G. W. R.

An Equilibrated Sterilisable Fluid of Physiological Hydrogen-ion Concentration. ALFRED FLEISCH (*Arch. exp. Path. Pharm.*, 1922, 94, 22—27).—The fluid has certain advantages over Ringer's or Tyrode's solutions. It possesses a constant P_H value of 7.52 at 37°, is isotonic with blood, is sterilisable, and contains potassium and calcium in a ratio which approximates to that in arterial blood. A similar relation exists between the total univalent and bivalent positive ions. The stock solution has the composition: sodium chloride, 10.5 grams; potassium chloride, 0.5 gram; calcium chloride, 0.3 gram; magnesium chloride, 0.1 gram; 5 c.c. of *N*-phosphoric acid, and 50 c.c. of water. This requires filtering. For use, 50 c.c. of the stock solution are mixed

with 1 litre of water, heated, and, after cooling, saturated with oxygen. Five c.c. of sterile *N*-sodium carbonate solution are then added. The heating may be omitted if a sterilised solution is not required. Modifications may be made to give fluids either richer or poorer in carbon dioxide.

E. S.

[Imperfect Digestion and] the Amino-acid Fractions and Hippuric Acid in the Urine of Pellagrins. J. R. MURLIN (*U.S. Public Health Service, Hygienic Lab. Bull.*, 1920, No. 116, 45—72).—The imperfect gastric digestion, established in 50—60% of the cases of pellagra, might be expected to lead to imperfect assimilation of protein material and the production of toxic imperfectly resolved substances which might be eliminated in part unchanged in the urine. It is clearly suggested, by comparison of two subjects, one without free acid and pepsin in the stomach and the other with normal gastric juice, that the quantity of formol-titration nitrogen in the urine may depend on gastric conditions. The quantity of hippuric acid excreted by pellagrins, especially those kept on a maize-vegetable diet, is from twice to three times the quantity excreted by normal men on a general mixed diet. This may denote an intestinal condition capable of producing toxins which may have far-reaching somatic effects.

CHEMICAL ABSTRACTS.

Products of Prolonged Tryptic Digestion of Casein. SIGMUND FRÄNKEL and PAUL JELLINEK (*Biochem. Z.*, 1922, 130, 592—603).—When casein is digested with trypsin until the bromine reaction is negative for tryptophan, the filtrate after precipitation with Hopkins's reagent gives on removal of mercury and addition of alcohol racemic hydroxyproline in 0.8% yield. From the filtrate mercuric chloride precipitates *histidine unhydride dihydrochloride*, decomp. 285°, in minute quantity. The mercuric chloride precipitate from alkaline solution, however, contained ammonium chloride and methylamine hydrochloride. The presence of the latter is attributed to a decarboxylase action of the tryptic ferment on glycine.

H. K.

Observations on Sugar Synthesis. II. An Abnormal Disturbance of Carbohydrate Exchange and its Relation to Diabetes Mellitus. RICHARD WAGNER and J. K. PARNAS (*Z. ges. exp. Med.*, 1921, 25, 361—384; from *Chem. Zentr.*, 1922, i, 893; cf. this vol., i, 487).—Further data are given with regard to the carbohydrate metabolism in a child with chronic interstitial hepatitis. Thyreoidin caused an increase in blood-sugar and a depression of acetone production, accompanied, however, by lipæmia, lipuria, and steatorrhœa. The production of sugar by degradation of body protein is held to be conditioned by thyroid activity, which is itself held in check by the pancreas as well as by mobilisation of liver carbohydrate. Conversely, excessive thyroid activity exerts an inhibitory effect on the pancreas.

G. W. R.

Effect of Radiothorium on Metabolism. K. MIYADERA (*Deut. med. Woch.*, 1922, 48, 252—253; from *Chem. Zentr.*, 1922, i, 1049).—A single injection of radiothorium into the blood-stream causes a gradual disturbance of metabolism resulting in an increase in the total nitrogen output in urine and faeces and also in the excretion of uric acid. These changes are attributed to increased protein decomposition and decreased nitrogenous anabolism. Oxidative processes are also intensified. G. W. R.

Animal Calorimetry. XXII. The Production of Fat from Protein. H. V. ATKINSON, DAVID RAPPORT, and GRAHAM LUSE [with G. F. SODERSTROM and JAMES EVENDEN] (*J. Biol. Chem.*, 1922, 53, 155—166).—From measurements of the respiratory quotient of dogs, it is concluded that, when the glycogen reservoirs of the body are full, the ingestion of large amounts of meat is followed by the production of fat from protein. E. S.

Lung Stones. A. SCHERER (*Beitr. klin. Tuberculose*, 1921, 49, 17—27).—The chief constituents of lung stones are calcium carbonate and phosphates; magnesium carbonate, magnesium phosphate, fats, cholesterol, and traces of silicates are also present. CHEMICAL ABSTRACTS.

Degradation of Bile Pigments by Anaerobic Putrefactive Intestinal Bacteria. FRITZ PASSINI (*Wiener klin. Woch.*, 1922, 35, 217—219; from *Chem. Zentr.*, 1922, i, 1057—1058).—Putrefactive anaerobic intestinal bacteria rapidly break down biliverdin and bilirubin. Formation of urobilinogen or urobilin was not observed. Presence of sugar does not prevent the decomposition of bile pigments by typical putrefying bacteria. Anaerobic fermentative bacteria have no effect on the bile pigments in substrates containing sugar. It is supposed that bile pigments are unaltered in those parts of the intestine where bacterial decomposition is mainly fermentative, their decomposition being confined to those parts where putrefactive action is predominant. G. W. R.

The Effects of Adrenal Feeding on the Iodine Content of the Thyroid Gland. E. M. BLACK, M. HUPPER, and J. ROGERS (*Amer. J. Physiol.*, 1922, 59, 222—226).—The addition of various preparations of adrenal glands (ox) to the dietary of dogs causes an increase in forty-five days of 50.7—70.4% in the iodine content of the thyroid gland. The effect appears to be chiefly due to a substance other than adrenalin. CHEMICAL ABSTRACTS.

Probable Occurrence of Proteinogenic Amines in the Thyroid. UBALDO SAMMARTINO (*Biochem. Z.*, 1922, 131, 219—225).—From 3 kilos of fresh thyroid glands, the author has isolated a trace of histamine picrate, tyramine picrate, and phenylethylamine picrate, as well as inositol. At an intermediate stage of the process of isolation, benzylation of the purified alcoholic extract was resorted to and the insoluble benzoylated products isolated and hydrolysed. In a shorter process, avoiding benzylation and using 400 grams of fresh horse thyroid and working very quickly

inositol was again isolated, but only potassium picrate and an unidentified picrate with m. p. above those of the picrates of the proteinogenic amines. H. K.

Keratin. I. A. HEIDUSCHKA and E. KOMM (*Z. physiol. Chem.*, 1922, **121**, 221—230).—Horn-clippings were heated at atmospheric pressure, in a vacuum, in sealed vessels, and with water or ammonia in sealed vessels. The temperature of initial partial degradation varies with the time of heating and the conditions of the experiment. Among the volatile products are hydrogen sulphide, ammonia, and sulphur compounds. H. K.

Beef Bone Fat and Neat's Foot Oil. HANNS ECKART (*Z. Unters. Nahr. Genussm.*, 1922, **44**, 1—29).—A table of analytical constants of bone fats, marrow fats, kidney fats, and neat's foot oils obtained from a well-nourished animal and as found in commerce is given. The rate of increase in free fatty acids shown by bone fat and neat's foot oil on storage depends on the conditions of storage, and is much more rapid if the sample is exposed to the action of light and air than if it is stored in the dark and sealed up. In the case of the solid fat exposed to light and air, an autocatalytic hydrolysis appears to take place whilst in the case of the oil the hydrolysis appears to be a unimolecular reaction. Measurements of the surface tension of neat's foot oil by the drop-pipette method gave values varying from 26.7 to 29.7 dynes/cm.² at 50°, according to the sample. The mixed ethyl esters of the fatty acids from bone fat were prepared and their analytical constants recorded. The compositions of beef bone fat and neat's foot oil are as follows: stearic acid, 19—21% and 2—3%; palmitic acid, 20—21% and 17—18%; oleic acid, 53—59% and 74.3—76.5%; glycerol, 5—10% in both cases; unsaponifiable substances, about 0.5% and 0.1—0.5%, respectively. The presence of cholesterol in the unsaponifiable substances was confirmed. Tristearin was definitely obtained as a constituent of beef bone fat. H. C. R.

Urinary Acidity. I. Some Effects of Drinking Large Amounts of Orange Juice and Sour Milk. N. R. BLATHERWICK and M. LOUISA LONG (*J. Biol. Chem.*, 1922, **53**, 103—109).—Orange juice produced alkaline urines with an increased organic acid and a decreased ammonia content; lactic acid milk, however, caused strongly acid urines due to an increased excretion of acid phosphate. No increase in the organic acid content of the urine was observed in the latter case. E. S.

Urine Iron, and Renal Function. RUDOLF EHRENBURG and ALFRED KARSTEN (*Pflüger's Archiv*, 1921, **193**, 86—92; from *Chem. Zentr.*, 1922, i, 650).—With moderate output of urine, the excretion of iron in man is smaller with large amounts, and larger with small amounts of urine eliminated; for example, 0.5 mg. in 1000 c.c. and 1.9 mg. in 500 c.c. per day. The amount excreted is a measure of total renal activity. G. W. R.

Periodicity in Chloride Excretion during Dropsical Nephritis. P. L. VIOLLE (*Compt. rend. soc. Biol.*, 1922, 86, 362—363; from *Chem. Zentr.*, 1922, i, 1052).—In dropsical nephritis with marked retention of chlorides, the excretion of sodium chloride is constant, independently of the water balance. When the kidneys again become permeable to chlorides, variations in the daily output of chlorides occur.
G. W. R.

Theory of the Retention and Excretion of Absorbed Bromine Salts, and the Halogen Content of the Organism. FR. BAUR and E. OPPENHEIMER (*Arch. exp. Path. Pharm.*, 1922, 94, 1—21).—The known facts concerning the retention and excretion of bromides are explained by the assumptions that the organism is in halogen equilibrium and that the ratio of chloride to bromide in the urine is the same as that in the organism. Using these assumptions, expressions are deduced which give, in terms of the original chloride content of the organism, the amount of bromide and chloride which will be excreted on any day following the administration of one or several similar daily doses of bromide. These expressions may also be used to calculate the chloride content of the organism.
E. S.

Fate of certain Sulphur Compounds when Fed to the Dog. CARL L. A. SCHMIDT and GUY W. CLARK (*J. Biol. Chem.*, 1922, 53, 193—207).—Estimations were made of the sulphur and amino-nitrogen content of the urine following the administration of certain sulphur compounds. The following conclusions are drawn from the results: Cysteic acid is deaminised but is otherwise unattacked during its passage through the animal organism. In agreement with the results obtained with man (A., 1920, i, 510), taurine does not combine with urea to form taurocarbamic acid, neither is its sulphur oxidised to any appreciable extent. The administration of isethionic acid does not lead to an increase in urinary sulphates. The greater part of the cystine absorbed undergoes oxidation. Urine is not a channel for the elimination of bile acids taken by the mouth. Appreciable amounts of sulphurous and thiosulphuric acids were found in the urine only after the ingestion of large quantities of sodium thiosulphate.
E. S.

Genesis of Thiosulphuric Acid in Animals. SERAFINO DEZANI (*Arch. Farm. sperim. Sci. aff.*, 1922, 33, 76—80, 81—91, 97—109).—The author discusses previous work on this subject, methods for detecting and estimating thiosulphuric acid in urine, and the various hypotheses which have been advanced to explain the occurrence of this acid in the animal organism. Salkowski's method for estimating thiosulphuric acid (A., 1914, i, 455) leads to erroneous results.
T. H. P.

Fat Excretion. ELSIE HILL and W. R. BLOOR (*J. Biol. Chem.*, 1922, 53, 171—178).—The amount and composition of the fat in the faeces are to a large extent independent of the diet. These results favour the idea of a fat excretion from the intestine.
E. S.

Cholesterol in Cerebrospinal Fluid. STANISLAO FABRIS (*Pediatrics*, 1921, 29, 1057—1064; *Ber. ges. Physiol.*, 11, 322; from *Chem. Zentr.*, 1922, i, 1058).—In normal children, 0.01% of cholesterol was found in cerebrospinal fluid. In hydrocephalic cases, cholesterol was absent, whilst in tubercular meningitis increased amounts were found.
G. W. R.

Scorpion Venom. WM. H. WILSON (*Bull. inst. Egypte*, 1921, 3, 67—73).—An examination of the venom of *Prionurus citrinus* and *Buthus quinque-striatus*. The former has d 1.903, and contains 6.5% of mineral salts and 13.7% of other solid material, chiefly protein. It consists of a clear plasma containing numerous refractile granules of two types; solubility and precipitation reactions are described. In contrast with the venom of spiders and snakes, the activity of that of *P. citrinus* is not destroyed by putrefaction.

CHEMICAL ABSTRACTS.

The Wax of Corpses. S. GOY and E. WENDE (*Biochem. Z.*, 1922, 131, 8—12).—The wax of two corpses buried five and one and a half years, respectively, consisted essentially of free fatty acids, free glycerol being present in very small quantity. A certain amount of the free fatty acids had become converted into calcium, magnesium, and ammonium soaps.
H. K.

Acetonuria of Diabetes. ROGER S. HUBBARD and SAMUEL T. NICHOLSON, jun. (*J. Biol. Chem.*, 1922, 53, 209—230).—Based on certain assumptions, a formula has been developed by means of which the molecular ratio of ketogenic to antiketogenic substances in the diet of diabetic patients may be calculated. From a study of a number of cases, it has been found that acetone excretion varies inversely as the value of this ratio. The excretion of acetone is sometimes increased by the inclusion of additional fat in the diet, although the extra fat theoretically replaces fat which the patient had been drawing from his own reserves.

E. S. S.

Acute Yellow Atrophy of the Liver. MAX KAHN and JOSEPH BARSKY (*Arch. int. med.*, 1921, 28, 142—150; *Ber. ges. Physiol.*, 11, 303—304; from *Chem. Zentr.*, 1922, i, 991).—In acute yellow atrophy of the liver, the tissue shows a very high water-content and an increase in ash, particularly soluble constituents, chlorine, sulphur, and magnesium. Calcium, iron, and silicon show a decrease. The content of fat varies; lecithin, phosphatides, and sulphotides show decreases.
G. W. R.

Sugar Regulation in Paralysis Agitans. K. DRESEL and F. H. LEWY (*Z. ges. exp. Med.*, 1922, 26, 95—103; from *Chem. Zentr.*, 1922, i, 897).—After administration of sucrose in paralysis agitans, blood-sugar remains normal for one and a half hours, but ultimately rises above the normal. After administration of dextrose, blood-sugar remains longer at a maximum than in normal cases.
G. W. R.

Effect of Primary Sodium Phosphate on Body Power. HERBERT HERXHEIMER (*Klin. Woch.*, 1922, 1, 480—483; from *Chem. Zentr.*, 1922, i, 985—986).—Phosphoric acid given as sodium dihydrogen phosphate has a favourable effect on growth and energy production. G. W. R.

The Effect of Adrenaline on Healthy Individuals. ALFRED BJURE and JOHN SVENSSON (*Uppsala läkareförenings förhandlingar*, 1921, 26, 36 pp.; *Ber. ges. Physiol.*, 11, 319; from *Chem. Zentr.*, 1922, i, 988).—Adrenaline, either in intramuscular or subcutaneous injections, produces increase in blood pressure and pulse frequency. Sugar in the urine does not increase, although an increase in blood sugar occurs. The absolute amount of sodium chloride excreted in the urine increases, although the sodium chloride content of the urine decreases. G. W. R.

Behaviour of 5-Iodoguaiacol in the Human Organism. ITALO SIMON (*Arch. Farm. speriment.*, 1922, 33, 133—144).—5-Iodoguaiacol, administered gastrically, produces little effect in the animal organism. In the rabbit, a dose of 0.64 gram per kilo. causes no inconvenience; in the dog, 0.83 gram per kilo. leads only to slight albuminuria; in man, 0.25 gram per kilo. produces no harmful phenomenon, and 1 gram only transient diarrhoea. The compound is partly absorbed by the gastro-enteric tube and partly expelled with the faeces. A dose of 0.08 gram per kilo., administered to a dog, is eliminated in the urine in combination with sulphuric acid, whilst with a dose of 0.83 gram union occurs also with glyceronic acid. The elimination takes place rapidly. T. H. P.

Choline as Hormone of Peristalsis. K. ARAI (*Pflüger's Archiv*, 1922, 193, 359—395; from *Chem. Zentr.*, 1922, i, 889).—In experiments with cats suffering from artificially induced peritonitis, peristalsis was produced by administration of choline chloride (0.01 gram per kilo.). G. W. R.

The Nature of Specific Poisons. PETER BERGELL (*Z. physiol. Chem.*, 1922, 121, 231—239).—The author has investigated the question as to whether an animal dosed with tropine is especially sensitive to tropic acid, and, conversely, when dosed with tropic acid is sensitive to tropine, these components of the toxic alkaloid atropine being individually relatively harmless. Mice readily become acclimatised to tropine or tropic acid. After the injection of a succession of small doses of either of these substances, a subsequent injection of the other substance leads to death or very severe illness. H. K.

Physiology and Pharmacology of the Leech, *Hirudo medicinalis*. WERNER TESCHENDORF (*Pflüger's Archiv*, 1921, 192, 135—162; from *Chem. Zentr.*, 1922, i, 893).—The musculature of the leech is comparatively little affected by an induction current, by variations in osmotic pressure, or by inorganic substances. It is sensitive to alkaloids, for example, nicotine. Small variations in hydrogen-ion concentration have little effect on the tonus; alcohol and chloroform increase tonus. G. W. R.

Chemistry of Vegetable Physiology and Agriculture.

Denitrification with Formates. Influence of the Kation. J. GROENEWEGE (*Bied. Zentr.*, 1922, **51**, 219—220).—With *Bacterium denitroformicum*, n. sp., using calcium formate as the exclusive source of carbon, denitrification does not take place in culture solutions containing potassium monohydrogen phosphate owing to reaction with the calcium formate whereby calcium phosphate and free formic acid are produced. When the culture-solution is maintained neutral or slightly alkaline, denitrification takes place only on aëration. If, however, the calcium formate is replaced by potassium or sodium formate, denitrification takes place even under anaerobic conditions. G. W. R.

Fermentation of Hexoses and Related Compounds by Certain Pentose-fermenting Bacteria. W. H. PETERSON, E. B. FRED, and J. A. ANDERSON (*J. Biol. Chem.*, 1922, **53**, 111—123).—The action on various sugars of four cultures of the group of pentose-fermenting organisms previously described (this vol., i, 201) has been determined. Dextrose, lævulose, lactose, raffinose, and melczitose were converted almost quantitatively into lactic acid, small quantities of carbon dioxide, which is regarded as a product of cell respiration, also being produced. With the last three sugars, the action was slow, and, when the cultures became old, a secondary fermentation began with the production of volatile acids. Mannitol was fermented differently from the sugars, thus showing the influence of the terminal alcohol group. With one exception, in which no volatile acids were formed, the products from this substance were lactic acid, ethyl alcohol, formic acid, and acetic acid. The action of the pentose-fermenting bacteria resembles that of *Streptococcus lactis*. The lactic acid produced by the former, however, is always optically inactive whereas that produced by the latter is active. E. S.

The Acetone and Butyl Alcohol Fermentation of Various Carbohydrates. GUY C. ROBINSON (*J. Biol. Chem.*, 1922, **53**, 125—154).—The fermentative ability of an organism of the *Granulobacter* type, isolated from a sample of fresh barley, towards various carbohydrates was studied. The course of fermentation was followed by making periodic estimations of the titratable acidity of the media and of the amount and, where possible, the composition of the carbohydrates present. The carbohydrates studied fell into two groups, according to the type of fermentation which occurred. In the first group, which consisted of dextrose, lævulose, mannose, sucrose, lactose, and starch, the acidity of the media, after reaching a maximum, showed a decided fall, whilst the carbohydrate was completely consumed. The second group comprised galactose, xylose, arabinose, raffinose, melczitose, inulin, and mannitol. In these cases, the high acidity persisted and the consumption was incomplete. Dextrin* fell into the first or second

group, according as it was prepared by malt amylase hydrolysis or acid hydrolysis of starch. Trehalose, rhamnose, melibiose, and glycerol were not fermented. With mixtures containing dextrose and either sucrose or lactose, dextrose was preferentially consumed. Maltose, however, was fermented concurrently with dextrose, lævulose, or mannose. Galactose was more completely consumed in the presence than in the absence of dextrose. From the experimental data, it is concluded that the organism secretes the enzymes amylase, inulinase, and maltase, but not sucrase, lactase, or raffinase. Raffinose is hydrolysed to melibiose and lævulose by sucrase within the cell.

E. S.

Decomposition of Inositol and Glycerol after the Manner of True Sugars by *Bacillus lactis aerogenes*. H. KUMAGAWA (*Biochem. Z.*, 1922, **131**, 157—160).—In presence of calcium carbonate and calcium sulphite, inositol is degraded by *B. lactis aerogenes* with production of acetaldehyde, lactic acid, and succinic acid. Glycerol gives acetaldehyde.

H. K.

The Action of Tribromoxyleneol on the Tubercle Bacillus. (Mlle.) T. DUBOC (*Compt. rend.*, 1922, **175**, 326—328).—Emulsions of bovine, avian, and human tubercle bacilli were treated with tribromoxyleneol. Part of the organisms was absorbed at once; the remainder formed a yellow, frothy layer on the surface of the liquid, gradually disappearing as the liquid cleared. After periods of nineteen to one hundred and forty-five days, varying with the nature and previous history of the organisms, all bacilli had disappeared and the liquid remained perfectly clear. Microscopic examination of organisms, periodically removed from treated emulsions, showed the gradual disappearance of acid-fast organisms, loss of structure, and finally complete solution.

A. G. P.

Accelerators of Fermentation. HANS VON EULER and SIGNE KARLSSON (*Biochem. Z.*, 1922, **130**, 550—555).—Washed dry yeasts, free from co-enzyme, are not activated by juices and extracts containing much vitamin-B, but there is a marked acceleration of fermentation by washed dry yeast on addition of the co-enzyme.

H. K.

Influence of Mineral Spring Water on the Carbohydrate Interchange in Yeast. PAUL MAYER (*Biochem. Z.*, 1922, **131**, 1—5).—The use of Karlsbad water as solvent for the sucrose in yeast fermentation leads to an increased production of glycerol and diminished production of alcohol. Solutions made up from Karlsbad salts (powder form), show this effect to an enhanced degree.

H. K.

The Influence of Thyroxin on Alcoholic Fermentation. M. TOMITA (*Biochem. Z.*, 1922, **131**, 175—177).—Thyroxin has a slight, stimulating action on alcoholic fermentation.

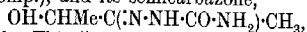
H. K.

Production of the Second and Third Forms of Fermentation with *Saccharomyces Saké*, *Zygosaccharomyces major*, and *Z. salus*. H. KUMAGAWA (*Biochem. Z.*, 1922, **131**, 148—156).—The Japanese yeasts named can ferment sugar according to

the second and third modes. *Saccharomyces Saké* can withstand a greater proportion of sodium hydrogen sulphite than German yeasts, with the resultant production of increased yields, 19.6% of acetaldehyde, and 39.2% of glycerol, whilst the alcohol production was only 10%.

H. K.

Carboligase. V. The Binding of Carbon to Carbon Biosynthetically in the Aliphatic Series. JULIUS HIRSCH (*Biochem. Z.*, 1922, **131**, 178—187).—Yeast fermentation in presence of pyruvic acid leads to the production of optically active acetylmethylcarbinol, which is isolated and identified by its phenyllosazone, m. p. 241—242°, its *p*-nitrophenyllosazone, m. p. 308—310° (decomp.), and its semicarbazone,



m. p. 193—194°. This "acyloin" condensation is brought about by the carboligase.

H. K.

Ammonia as a Product of Protein Transformation caused by Mould Fungi and the Conditions of its Formation. V. S. BUTKEVICH (*Rec. d'articles dédiés au Prof. C. Timiriazev*, 1916, 457—499; *Abstracts Bact.*, **4**, 36).—The different species of fungi vary as regards their capacity to decompose proteins with formation of ammonia. The mould fungi are capable of utilising for the formation of ammonia not only amino- but also the amido-complexes. Both these reactions were studied, with the mycelium and with the expressed juice of *Aspergillus niger*. This fungus contains an enzyme which is capable of transforming the amido-group of asparagine into ammonia. An alkaline medium is most favourable for its action. The ammonification of the amino-group of amino-acids can only be observed with living cells.

CHEMICAL ABSTRACTS.

Formation of Citric and Oxalic Acids in *Citromyces* Cultures on Sugar and a Process for the Estimation of these Acids. WL. BUTKEWITSCH (*Biochem. Z.*, 1922, **131**, 327—337).—Various kinds of *Citromyces* were cultivated on 10% sucrose solutions deficient in nitrogen, and calcium carbonate was added. Citric and oxalic acids were formed, and were estimated. In each case, a large yield of oxalic acid means a diminished yield of citric acid, and vice versa. This is due to the formation of oxalic acid at the expense of the citric acid. These two acids may be estimated when present together in an approximately quantitative manner either (1) by extraction of the mixed calcium salts with dilute hydrochloric acid, or (2) by dissolving the salts in hydrochloric acid and adding sodium acetate which precipitates calcium oxalate alone. The main discrepancy falls on the citrate.

H. K.

Utilisation and Formation of Citric Acid in Cultures of *Citromyces glaber* on Sugar. WL. BUTKEWITSCH (*Biochem. Z.*, 1922, **131**, 338—350).—Citric acid is formed by *Citromyces glaber* when grown either on normal or on abnormal media. If citric acid or citrates be added to the nutrient media, oxalic acid

appears directly. In dilute solution, the "economic coefficient" of the utilisation of citric acid approaches that of dextrose, but in concentrated solutions it falls off. The combination dextrose-citric acid stimulates the productive metabolism.

H. K.

Action of Selenium on the Metabolism of Plants in Presence of the Radioactivity of Air and of Soil. JULIUS STOKLASA [with P. KŘÍČKA, J. PĚNKAVA, J. ZELENKA, J. CHMELÁK, and V. JÁNSKÝ] (*Biochem. Z.*, 1922, **130**, 604—643; cf. this vol., i, 613, 614).—The authors have investigated the action of ions containing selenium in the presence and absence of radium emanation on (a) the growth of azotobacter, (b) the germination of seeds, and (c) the development of plants. Sodium selenite is found to inhibit the growth of *Azotobacter chroococcus* but this inhibition is to some extent overcome by radium emanation. On the germination of seeds, both sodium selenite and selenate are detrimental, the selenite being the more powerful. Radioactive air accelerates the growth of seeds and inhibits the toxic action of selenites and selenates. A parallel behaviour is observed on the growth of plants, except that very minute quantities of selenates may stimulate growth.

H. K.

The Diastatic Value of Malt. FR. DUCHÁČEK (*Chem. Listy*, 1922, **16**, 202—207).—The importance, in post-war brewing, of knowing the diastatic value (determined by the method of Windisch, *Woch. Brau.*, 1921, **38**, 149) of the malt used, is pointed out, and this value is given for numerous samples of last year's malt production in Czechoslovakia. From a comparison of the chemical and physical properties of these samples, it is concluded that none of these can alone allow of the estimation of the diastatic value of the sample in question, but that this value is more affected by the procedure in the germinator and in the malt-kiln. Particularly on the upper shelf of the latter is the diastase apt to be destroyed by inefficient drying, whilst efficient drying will sometimes double the diastatic value of a malt.

R. T.

The Presence of the Antineuritic Substance, Water-soluble B, in Chlorophyll-free Plants. C. R. ORTON, E. V. MCCOLLUM, and NINA SIMMONDS (*J. Biol. Chem.*, 1922, **53**, 1—6).—Vitamin-B is present in small quantities in onion roots; it is therefore concluded that this vitamin is not associated with the chloroplasts in plant-tissue. The mushroom, *Agaricus campestris*, is a good source of vitamin-B; experiments with Indian-pipe, *Monoctropa uniflora*, gave inconclusive results, whilst *Gronovius's* dodder, *Cuscuta Gronovii*, could not be tested owing to its toxic properties.

E. S.

Preparation and Properties of Vitamin-B. SOGEN TSUKUNE (*Biochem. Z.*, 1922, **131**, 124—139).—The author has prepared an active vitamin-B preparation from an 80% alcoholic extract of 30 kilos of rice polishings and from an aqueous extract of 4 kilos. After cleansing with basic lead acetate, the vitamin is precipitated by phosphotungstic acid and the precipitate decomposed by barium

hydroxide. After removal of excess of barium hydroxide, a precipitation is effected in acid solution with silver and the filtrate made weakly alkaline with barium hydroxide, whereupon a second silver fraction is obtained containing the vitamin. The vitamin preparation is precipitated by tannin and picric acid and the picrate is soluble in alcohol and hot water. It is not soluble in the neutral state in alcohol of more than 80% strength, but is readily soluble in acidified alcohol and in water. H. K.

Glacial Acetic Acid as a Solvent for the Antineuritic Substance, Water-soluble B. VICTOR E. LEVINE, E. V. MCCOLLUM, and NINA SIMMONDS (*J. Biol. Chem.*, 1922, 53, 7—11).—Glacial acetic acid is a good solvent for the extraction of vitamin-B from plant material. Impurities can be largely removed from such extracts by precipitation with ether. E. S.

Chemical Constituents of Green Plants. XIX. Occurrence of Lactic Acid and Succinic Acid in the Leaves of the Raspberry (*Rubus idaeus*). HARTWIG FRANZEN and EMMI STERN (*Z. physiol. Chem.*, 1922, 121, 195—220).—The aqueous extract of raspberry leaves, after removal of substances precipitable by lead acetate, contains chiefly magnesium, calcium, and manganese salts of lactic acid with a little succinic acid. The content of lactic acid in the dried leaves is 1%. The isolation and characterisation of these acids is facilitated by fractionation of the esters, conversion into hydrazides, and condensation with benzaldehyde. H. K.

Nutmeg Butter. H. B. (*Mat. grasses*, 1922, 14, 6099).—Nutmeg butter is composed of 1% butyric, 19% oleic, and the remainder myristic. It has m. p. 31°.

CHEMICAL ABSTRACTS.

The Presence of Cobalt and Nickel in Arable Soil. GABRIEL BERTRAND and MOKRAGNATZ (*Compt. rend.*, 1922, 175, 112—114).—In two samples of arable soils the authors have found respectively 0.00028% of cobalt and 0.00136% of nickel, and 0.00037% of cobalt and 0.00174% of nickel. W. G.

The Effect of Lime, Leaching, form of Phosphate, and Nitrogen Salt on Plant and Soil Acidity, and the Relation of these to the Feeding Power of the Plant. F. C. BAUER and A. R. C. HAAS (*Soil Sci.*, 1922, 13, 461—480).—Soja-beans and maize were grown in sand cultures with suitable nutrient solutions and the rates of growth, together with the hydrogen-ion concentrations of the juices of various parts of the plants were compared. Limestone treatment, leaching, and the nature of the phosphate and nitrogen salts applied produced considerable effects on the acidity of the nutrient medium and of the plant juices. The acidity was closely related to the growth and feeding power of the plants. Limestone, by reducing soil acidity, reduced also the acidity of soja beans grown in the soil. In a few cases increased vigour of the plants resulted from liming and this was accompanied by increased acidity of the plant juices. The increased acidity of the nutrient medium by leaching usually resulted in increased

acidity of the juices of maize plants. Acid phosphates raised the acidity of the medium and of the plant juices more than did rock phosphates. The availability of rock phosphate to the plant increases with greater acidity of the medium. Ammonium nitrate increased the acidity of the soil and of the root juices of maize more than did sodium nitrate, but there was little difference apparent in the juices of the upper portions of the plants. The total acidity of soja-bean roots did not increase with increasing actual acidity. On the other hand, the total acidity of the maize plant increased with the actual acidity of the juices of both roots and tops. The total acidity of maize tops was usually greater than that of the roots. Sodium nitrate produced greater acidity than ammonium nitrate in maize tops. Limestone reduced the actual acidity of soja bean nodules below that of the roots on which they grew. Variations in the acidity of soja-bean nodules due to liming followed those of the juices of the upper portions of the plant.

A. G. P.

Acid Soils. III. The Influence of Calcium Carbonate, Calcium Oxide, and Calcium Sulphate on the Soluble Soil Nutrients of Acid Soils. R. H. ROBINSON and D. E. BULLIS (*Soil Sci.*, 1922, 13, 449—460).—The acid soils examined responded very differently in field trials, when limed to the requisite extent to satisfy the Veitch "lime requirement." Examination of the water-soluble constituents of laboratory samples showed the chief difference to be a rapid formation of nitrates in those soils which responded to lime in the field. Treatment with calcium sulphate increased the soluble potassium and magnesium in all soils. [See also *J. Soc. Chem. Ind.*, 1922, 677A].

A. G. P.

Influence of Salts on Azofication in Soil. J. E. GREAVES, E. G. CARTER, and YEPPA LUND (*Soil Sci.*, 1922, 13, 481—499).—Soil was treated with varying amounts of the chlorides, sulphates, carbonates, and nitrates of sodium, potassium, magnesium, calcium, iron, and manganese, and their effects on the rate of nitrogen fixation were compared. The toxicity of the salts is specific, and is not governed by the electronegative ion. All the salts examined were less toxic to the nitrogen-fixing organisms than to the nitrifiers or ammonifiers. The toxic quantity of any particular salt varied with the type of soil. No sodium salts were toxic in quantities up to 460 parts of sodium per million of soil. Potassium chloride and carbonate, manganese carbonate, and ferric sulphate did not stimulate nitrogen fixation under any conditions examined. All other salts had a stimulating effect. The common soil alkalis would not affect nitrogen-fixing organisms, even if present in sufficient quantities to retard ammonification, nitrification, and plant growth, provided the soil is not acid and contains the necessary nutrients. Nitrogen-fixing bacteria are much more resistant to the salts than are ammonifiers, nitrifiers, and many higher plants.

A. G. P.

Organic Chemistry.

The Ozonides of Petroleum. RUDOLF KOETSCHAU (*Z. angew. Chem.*, 1922, 35, 509—513; cf. Molinari and Fenaroli, A., 1908, i, 933).—A Texas transformer oil, d 0.915, was found to have a molecular weight of 293, whilst the ozonide, of which 25% was produced from the oil, had a molecular weight of 663. A solution of this ozonide in benzene, after keeping for a few hours, had a molecular weight of 606 only, and after two days a molecular weight of 479, showing that decomposition into compounds of lower molecular weight had taken place. The figure 663 corresponds closely with that of a dimeric diozonide (688). The molecular weights of mineral oils determined in camphor are generally lower than those determined in benzene. The ozonides from Texas and Pennsylvanian spindle oils have a characteristic pungent odour, and separate as white, flocculent precipitates, which gradually change to a red resin at temperatures of 20° and above. Oils poor in sulphur give more stable ozonides of a lighter colour. The curves of ozone absorption are very steep at their commencement, and the maximum increase of weight is 16—17%. "White oils" show no formation of ozonides, but a considerable increase in viscosity when exposed to the action of ozone.

The ozone value is subject to too great variations for employment in analysis, but a "splitting number" determined by taking the acidity of an ozonised oil which has been boiled for half an hour with water is of utility in the examination of used transformer oils.

H. M.

Hydrogenation of Unsaturated Hydrocarbons. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 350429; from *Chem. Zentr.*, 1922, ii, 1026).—In the hydrogenation of unsaturated hydrocarbons by passing them, mixed with hydrogen, over metallic catalysts, a better utilisation of the hydrogen is obtained by diluting with methane, ethane, or ethylene. For example, in the preparation of pure ethane from acetylene the mixture is diluted with ethane until the acetylene content of the mixture amounts to less than 30% by volume. Similarly, in the preparation of a mixture of ethylene and ethane the mixture is diluted with ethane or ethylene until the acetylene content is less than 35% by volume.

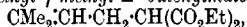
G. W. R.

The Formation of Butadiene from Ethylene. J. E. ZANETTI, J. R. SUYDAM, jun., and M. OFFNER (*J. Amer. Chem. Soc.*, 1922, 44, 2036—2041).—The formation of butadiene from ethylene has been studied at temperatures varying from 550° to 850° . The temperature of maximum formation has been shown to be 750° , above which the decomposition of ethylene into methane, hydrogen, and carbon occurs very rapidly. The maximum quantity of ethylene transformed into butadiene is 0.0096 litre per litre of ethylene.

It is suggested that the formation of aromatic hydrocarbons from ethylene takes place, at least in part, through the intermediate formation of butadiene. Attention is directed to the formation of an aliphatic hydrocarbon of higher boiling point from one of a lower boiling point and to the possible rôle of similar reactions in the cracking of oils.

H. W.

The Addition of Hydrogen Haloids to Isoprene. H. STAUDINGER, W. KREIS, and W. SCHILT (*Helv. Chim. Acta*, 1922, 5, 743—756).—When isoprene combines with 1 mol. of hydrogen bromide, addition takes place at the α - and δ -positions with formation of *dimethylallyl bromide* [α -bromo- γ -methyl- Δ^{β} -butene], $\text{CMe}_2\text{CH}(\text{CH}_2\text{Br})$, the constitution of which was established in the following manner. It condenses readily with sodium ethyl malonate, forming *ethyl γ -methyl- Δ^{β} -butenylmalonate*,



b. p. 127°/11 mm. When hydrolysed with alcoholic sodium hydroxide, this gives γ -methyl- Δ^{β} -butenylmalonic acid, m. p. 95°—96°. The fact that the crude acid has a sharp melting point proves that the compound of isoprene and hydrogen bromide is a uniform product. γ -Methyl- Δ^{β} -butenylmalonic acid when heated at 160° loses carbon dioxide with formation of *dimethylallylacetic acid* (δ -methyl- Δ^{γ} -hexenoic acid), a colourless oil, b. p. 103—105°/10 mm. The constitution of this compound is fixed by its oxidation with permanganate to the known δ -dimethyl- δ -hydroxylævulic acid and eventually into acetone and succinic acid.

The halogen of α -bromo- γ -methyl- Δ^{β} -butene is specially reactive, on account of the double bond in the $\beta\gamma$ -position. With guaiacol, it condenses in alcoholic sodium hydroxide solution to give *guaiacyl- γ -methyl- Δ^{β} -butenyl ether*, a viscous, nearly colourless oil, b. p. 140°/10 mm., which, by heating at 220°, changes into *p- γ -methyl- Δ^{β} -butenylguaiacol*, b. p. 148—149°/12 mm. The latter was methylated with methyl sulphate to *p- γ -methyl- Δ^{β} -butenylveratrole*, b. p. 140°/10 mm., which gave veratric acid on oxidation. The great reactivity of bromomethylbutene was shown by its behaviour with magnesium, when very little Grignard compound could be detected since it reacted almost at once with more of the bromide to form *tetramethyldiallyl* [$\beta\eta$ -dimethyl- $\Delta^{\beta\delta}$ -octadiene], b. p. 45—50°/11 mm. A similar reaction was observed by Rupe and Burgin (*A.*, 1910, i, 161) with styryl bromide. They also obtained, besides the normal distyryl, an isomeric compound which, from its oxidation products, must be a diphenylallyl, that is α , α -diphenyl- $\Delta^{\alpha\epsilon}$ -hexadiene, $\text{CHPh}(\text{CH}(\text{CH}_2\text{CHPh})\text{CH}(\text{CH}_2\text{CH}_2))_2$, not $\alpha\delta$ -diphenyl- $\Delta^{\alpha\epsilon}$ -hexene, as they supposed. Evidence was obtained of the formation of a second hydrocarbon, $\text{CMe}_2\text{CH}(\text{CH}_2\text{CMe}_2\text{CH}(\text{CH}_2))_2$, in a similar manner from α -bromo- γ -methyl- Δ^{β} -butene. The presence of this compound would account for the observed formation of dimethylsuccinic acid among the oxidation products of the mixed hydrocarbons obtained from bromomethylbutene and magnesium. With magnesium phenyl bromide, bromomethylbutene reacts to form γ -methyl- Δ^{β} -butenylbenzene. By the action of magnesium on

α -bromo- γ -methyl- Δ^8 -butenyl bromide in presence of carbon dioxide, a small quantity of pyroterebic acid was formed. E. H. R.

Isoprene Dibromide. H. STAULINGER, O. MUNTWYLER, and O. KUPFER (*Helv. Chim. Acta*, 1922, 5, 756—767).—The dibromide formed by addition of bromine to isoprene is $\alpha\delta$ -dibromo- γ -methyl- Δ^8 -butene, since on oxidation it gives bromoacetic acid. The compound therefore contains two reactive bromine atoms (cf. preceding abstract). Attempts to obtain a cyclopentene derivative by condensing it with sodium ethylmalonate were not successful. Only one atom of bromine reacted with the malonate, the other being lost as hydrogen bromide. The condensation product was not a uniform substance but appeared to consist principally of ethyl δ -methyl- Δ^6 -pentadiene- $\alpha\alpha$ -dicarboxylate. On reduction, it united with four atoms of hydrogen and the resulting ester, after hydrolysis, was converted into a monocarboxylic acid which was identified as δ -methylhexoic acid. The condensation product must consequently contain the ester, $\text{CH}_2\text{CMe}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})_2$. By hydrolysing the condensation product before hydrogenating, and distilling after removing carbon dioxide, there were obtained a methylpentadienecarboxylic acid and a lactone of a hydroxy-methylpentenecarboxylic acid which were not identified with certainty. The lactone may be that of γ -hydroxy- δ -methyl- Δ^6 -pentenecarboxylic acid; it is a colourless liquid, b. p. 105—110°/12 mm.; it is oxidised by permanganate or by hydrogen peroxide to succinic acid. Besides these two products were isolated a lactonic acid, m. p. 119—122°, giving a monoethyl ester, m. p. 85—86°, and a mixture of substances formed by the action of 1 mol. of isoprene dibromide on 2 mols. of ethyl malonate.

From isoprene tetrabromide was obtained a new *dibromoisoprene*, b. p. 78—83°/12 mm., a liquid of pleasant odour. *Isoprene dibromide*, from isoprene and bromine in carbon disulphide solution, is an unpleasant smelling liquid, b. p. 90—96°/12 mm., and has the constitution given above. When incompletely oxidised with permanganate, it forms $\alpha\delta$ -dibromo- $\beta\gamma$ -dihydroxy- β -methylbutane, $\text{CH}_2\text{Br}\cdot\text{CMe}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Br}$, m. p. 127°. From isoprene dibromide by treatment with alcoholic sodium methoxide was obtained a mixture of bromoisoprenes difficult to separate. Unlike isoprene itself, the mono- and di-bromoisoprenes do not polymerise to form caoutchouc-like products, but decompose when heated.

E. H. R.

Electrolytic Oxidation of Alcohols. I. isoAmyl Alcohol. SHUNZO KOIZUMI (*Mem. Coll. Sci. Kyoto*, 1922, 5, 359—382).—The material used in the investigation had b. p. 130—132°, d_4^{20} 0.811, and was obtained by fractional distillation of technical isoamyl alcohol; it possibly contained a small quantity of optically active amyl alcohol. The experiments were made in a divided cell, the cathode being of nickel gauze or sheet lead and the cathode solution being sulphuric acid or dilute sodium hydroxide solution. Lead peroxide acted most effectively as anode material. The products

of the oxidation were isovaleric acid, isovaleraldehyde, and carbon dioxide. In alkaline solution, the acid formed was always accompanied by the aldehyde; the current efficiency increased with decreasing current density. In a sulphuric acid solution, aldehyde was produced only when the current density fell below 1 amp. per 100 sq. cm. For the electrolytic preparation of isovaleric acid, the most suitable current density was found to be 1–1.4 amp./sq. dm., if the solution remained stationary and about 2 amp./sq. dm. when it was stirred. The most favourable concentration of sulphuric acid was 10–20%. The temperature should be maintained below 30°. Vanadium pentoxide, cerium sulphate, potassium dichromate, and ferrous sulphate were found to be effective oxygen carriers.

A convenient and rapid electrolytic method for preparing isovaleric acid without involving the use of a diaphragm is described in detail. H. W.

Preparation of Glycerol from Sugar. VEREINIGTE CHEMISCHE WERKE AKT.-GES. (D.R.-P. 343321; from *Chem. Zentr.*, 1922, ii, 1085).—The fermentation of sugar to form glycerol is carried out with addition of salts of acid or neutral reaction as well as nutrient salts. As examples of the salts added, ferrous sulphate, aluminium sulphate, ammonium chloride, and calcium chloride are mentioned. Ammonium sulphate, sodium phosphate, potassium sulphate, and magnesium sulphate are used as nutrient salts. The addition of neutral or acid salts increases the yield of glycerol. The yeast is also less harmfully affected than is the case in alkaline solution. G. W. R.

Preparation of Glycerol from Sugar. VEREINIGTE CHEMISCHE WERKE AKT.-GES. (D.R.-P. 347604; from *Chem. Zentr.*, 1922, ii, 1086).—In the formation of glycerol from sugar, the fermentation is allowed to reach its maximum intensity and, without interruption of the process, a further addition of sugar is made together with smaller amounts of yeast and nutrient salts than in the initial mixture. A larger yield of glycerol and a quicker fermentation are thereby obtained. In an example given, the yield of glycerol was 23% of the sugar used. G. W. R.

The Action of Epichlorohydrin on Normal Sodium Phosphate in Aqueous Solution and the Stability of a Diglyceromonophosphoric Diester. OCTAVE BAILLY (*Bull. Soc. chim.*, 1922, [iv], 31, 848–862; cf. A., 1921, i, 299, 493).—On attempting to prepare sodium α -glycerophosphate by using epichlorohydrin in place of the α -monochlorohydrin, the fact that one of the -ONa groups of the sodium phosphate behaves in a somewhat similar manner to the same group in sodium phenoxide (cf. Fourneau, A., 1910, i, 246) causes other reactions to take place simultaneously. When normal sodium phosphate is treated in aqueous solution with an equimolecular quantity of epichlorohydrin, formation of sodium monoglycidophosphate and diglycidophosphate occurs, and at the same time sodium α - γ -monoglycero-

monophosphate and $\alpha\gamma$ -monoglycerodiphosphate are formed. The two first-named substances are readily hydrolysed to α -glycerophosphate and $\alpha\alpha$ -diglyceromonophosphate, respectively. It is pointed out that the latter is extremely stable. An attempt was made to convert potassium diallyl phosphate into $\alpha\alpha$ -diglyceromonophosphate but this substance was only obtained in solution and in an impure condition; all attempts at crystallisation failed. Like the sodium salt, it is very stable and is not hydrolysed by prolonged boiling at 120° under pressure (cf. Fischer and Pfähler, A., 1920, i, 807). H. J. E.

Hydrolysis of $\beta\beta'$ -Dichlorodiethyl Sulphide. Synthesis of Divinyl Sulphide and the Preparation of a Non-vesicant Isomeride of $\beta\beta'$ -Dichlorodiethyl Sulphide. SIDNEY HARTLEY BALES and STANLEY ARTHUR NICKELSON (T., 1922, 121, 2137—2139).

Monothioethylene Glycol. GEORGE MACDONALD BENNETT (T., 1922, 121, 2139—2146).

The Constitution of Soap Solutions. Hexadecanesulphonic (Cetylsulphonic) Acid and other Sulphonates. MABEL HARRIET NORRIS (T., 1922, 121, 2161—2168).

Complex Compounds of Lead Acetate. R. WEINLAND and RUDOLF STROH (*Ber.*, 1922, 55, [B], 2219—2225).—A series of salts in which the lead-acetate ion functions in all probability as kation has been prepared by the action of perchloric or nitric acid on lead oxide and acetic acid or on lead acetate under conditions which are precisely described in the original. The kation is considered to be produced by the union of the lead atoms and the acetate residue by means of the subsidiary valencies of the oxygen

atoms thus, $\left[\text{Pb} \begin{array}{c} \text{O} \cdot \text{CMe} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{CMe} \cdot \text{O} \end{array} \right] \text{Pb}$ and $\left[\text{Pb} \begin{array}{c} \text{O} \cdot \text{CMe} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{CMe} \cdot \text{O} \end{array} \right] \text{Pb}$. The

salts are without exception beautifully crystalline. The perchlorate acetates explode violently when strongly heated or when struck; occasionally they appear to explode violently without obvious cause. Their electrical conductivity is in harmony with the conception that they are complex salts.

The following individual compounds have been prepared: The salt, $[\text{Pb}_2(\text{CH}_3\text{CO}_2)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, colourless, rhombic plates, formed by the action of perchloric and glacial acetic acids on a thin paste of lead monoxide and water; the salt, $[\text{Pb}_3(\text{CH}_3\text{CO}_2)_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, colourless, microscopic needles; the salt,

$[\text{Pb}_4(\text{CH}_3\text{CO}_2)_4](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, aggregates of needles or thick, hexagonal rods (this is the only salt of the series which can be crystallised unchanged from aqueous

solution); the salt, $[\text{Pb}_3(\text{CH}_3\text{CO}_2)_3](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CO}_2$, large, rhombohedral crystals; the salt, $[\text{Pb}_3(\text{CH}_3\text{CO}_2)_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, microscopic needles; the salt, $[\text{Pb}_2(\text{CH}_3\text{CO}_2)_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, small needles. H. W.

Complex Salt of Mercuric Acetate and Sulphide. A. MIOLATTI (*Gazzetta*, 1922, 52, ii, 27).—The compound, $\text{HgS.Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$, described by Bernardi and Rossi (this vol., i, 421), was prepared by Palm (1862) in another way, and is referred to in current handbooks. With other mercuric salts, such as the chloride or iodide, mercuric sulphide gives salts containing a complex kation of which the mercuric sulphide forms part (cf. Borelli, A., 1908, i, 515; ii, 1039; 1909, i, 452). T. H. P.

Saponification of Oils and Fats. H. M. LANGTON (*J. Oil and Colour Chemists' Assoc.*, 1922, 5, 41–75).—Large scale experiments were carried out on the hydrolysis of various oils and fats under a steam pressure of eight atmospheres, using 2.5% of the weight of oil of calcium or magnesium oxide as catalyst. The resulting curves obtained are of the exponential type in every case, the greater part of the oil or fat being hydrolysed in the first four hours and the velocity of the reaction thereafter falling to a very low rate. In most cases, magnesium oxide was more effective weight for weight than calcium oxide as a catalyst. H. C. R.

The Action of the Brush Discharge on Fatty Acids and their Glycerides. EGON EICHWALD (*Z. angew. Chem.*, 1922, 35, 505–506).—If oleic acid is subjected to the action of the brush discharge, the iodine value steadily falls, the mean molecular weight steadily rises, and stearic acid is produced. The increase in molecular weight per unit fall in iodine value increases from 6.3 at the beginning of the treatment to 43.5 after twenty-two hours' treatment. About 11% of the acid is converted into stearic acid in an atmosphere of air or nitrogen and 15% in an atmosphere of hydrogen. It is considered that the bombardment of the molecules causes hydrogen atoms to become detached in a highly active state, and that they immediately saturate the double bonds of other molecules of oleic acid, leaving some highly unsaturated molecules, which polymerise and cause the increase in molecular weight. Glycerides show similar effects under the brush discharge, the glyceryl part of the molecule being unaffected. The resulting polymerised oils have high viscosities and flat viscosity-temperature curves, and are of value as lubricants. Owing to the possibility of intramolecular saturation of double bonds in the case of glycerides, the increase in molecular weight in this case becomes even more apparent in the later stages of treatment than in the case of the free fatty acids. H. C. R.

The Transformation of Methyl α -Elæostearate into Methyl β -Elæostearate. R. S. MORRELL (*J. Soc. Chem. Ind.*, 1922, 41, 328r).—Polemical, pointing out that Bauer and Herberts (this vol., i, 806) failed to acknowledge the author's work (A., 1918, i, 372), in which it was shown that methyl α -elæostearate is transformed into the β -variety when distilled in a vacuum. E. H. R.

Brassicidic Anhydride, and Anhydridisation by means of Carbonyl Chloride. D. HOLDE and K. SCHMIDT (*Z. angew. Chem.*, 1922, 35, 502–503).—Brassicidic acid, brassidic anhydride,

and ethyl brassidate were prepared from erucic acid and its corresponding derivatives by isomerisation by means of nitrous acid. *Brassicidic anhydride* crystallises from alcohol in small needles, m. p. 64°, and gives the theoretical iodine value with the Hanus reagent. It has d_4^{20} 0.835. *Ethyl brassidate* forms leaflets, m. p. 30–30.5°, n_D^{20} 1.4587. The anhydrides of the fatty acids of train oil were prepared in an impure condition, containing chlorine, by the action of carbonyl chloride on their alkali salts. They formed pasty products of higher melting point than the corresponding glycerides and acids. The difference frequently observed between the acid and saponification values of the acids of fatty oils may possibly be explainable by the observation that they are often accompanied by a proportion of anhydrides, which, as in the case of erucic, brassidic, and other higher anhydrides, do not react normally with cold alcoholic hydroxide solutions. G. F. M.

Promoters of the Hydrogenation of Oils. I. SEICHI UENO (*J. Chem. Ind. Japan*, 1922, 25, 777–783; cf. *ibid.*, 1918, 21, 898, and 1920, 23, 1216).—In the hydrogenation of herring and cotton-seed oils with hydrogen, using nickel or nickel sulphate (0.3–0.5% as nickel) as a catalyst, the presence of 2–3% of palmitic, oleic, stearic, or benzoic acid promotes the reaction.

K. K.

Perilla Oil. K. H. BAUER and R. HARDEGG (*Chem. Umschau*, 1922, 29, 301–305).—Experiments were made to separate and identify the saturated and unsaturated fatty acids of perilla oil, obtained from the fruit of the East Asian labiate *Perilla ocymoides*. The oil had the following constants: d_4^{20} 0.9280; n_D^{20} 1.4830; saponification number, 187.4; iodine number, 204.0; mean hexabromide number, 50.8%. The m. p. of the hexabromide was 180°. The oil contained 12% of saturated and 88% of unsaturated fatty acids. By fractional precipitation of the magnesium salts and crystallisation of the acids from the different fractions, palmitic acid was identified in the saturated acids; a second saturated acid of higher m. p. than palmitic appears also to be present. The unsaturated acids were investigated by oxidising with cold potassium permanganate in alkaline solution and extracting the oxidation product with different solvents. From the water-soluble portion were obtained the two hexahydroxystearic acids, linusic acid, m. p. 201°, and isolinusic acid, m. p. 173–175°. From the water-insoluble portion was isolated a tetrahydroxystearic acid, m. p. 135–140°, which may be identical with the acid obtained by Nicolet and Cox through the dichloro- and dibromo-dihydroxy-stearic acids (this vol., i, 320).

Attempts were made to separate the mixed hexahydroxystearic acids by fractional crystallisation of the methyl esters. It was not possible in this way to separate linusic and isolinusic acids. By extraction of the mixed esters with ethyl acetate, however, an ester soluble in this solvent was obtained, m. p. 158–160°, which when hydrolysed gave what appears to be a new hexahydroxy-

stearic acid, m. p. 165°. *Methyl linusate* forms colourless, microscopic crystals, m. p. 195°. E. H. R.

Direct Oxidation of Esters of Hydroxy-acids by Oxygen or Air. L.-J. SIMON (*Compt. rend.*, 1922, 175, 489—491; cf. Fenton and Jones, T., 1900, i, 69; also Ciusa and Pioggiani, A., 1914, ii, 604).—Ethyl lactate is spontaneously oxidised in contact with air, ethyl pyruvate being formed. The action is slow in the cold, but is accelerated by shaking or by the influence of light. On heating in a current of air, this ester, and also the methyl, butyl, and amyl esters of lactic acid, yield the corresponding ester of pyruvic acid; after some hours, sufficient oxidation has taken place to admit of detection of methyl or ethyl pyruvate by the formation of phenylhydrazones, whilst in twenty-four to forty-eight hours the transformation has taken place to the extent of 5 to 10%. Rise of temperature facilitates the change, but after a certain point other and more complex reactions take place. In the case of butyl lactate, heating for twenty hours at 180° gave a yield of 9% of butyl pyruvate. A second oxidation reaction of ethyl lactate occurs at the ordinary temperature, the products being acetaldehyde and carbon dioxide; it is stated that this is one type of reaction which prevents larger yields of pyruvate being obtained. Direct oxidation of ethyl glycolate to ethyl glyoxylate has also been observed and the question is raised as to the generality of this reaction with α -hydroxy-acids. H. J. E.

Inorganic Complex Salts. Crystallographic and Optical Study. I. ISABEL ELLIE KNAGGS (T., 1922, 121, 2069—2079).

Preparation of Maleic Acid. CHARLES R. DOWNS (U.S. Pat. 1374720; from *Chem. Zentr.*, 1922, ii, 1055; cf. A., 1921, i, 216—217).—For the preparation of maleic acid, benzene in a state of vapour is mixed with a gas containing oxygen and passed over vanadium oxide, as catalyst, at about 400°. In order to limit the oxidation, a constant temperature is maintained by the dispersion of mercury vapour in the zone of reaction.

G. W. R.

Ethyl α -Cyano- β -methylglutaconate and its Methyl Homologues. EDWARD HOPE (T., 1922, 121, 2216—2223).

The Addition of Hydrogen Cyanide to Derivatives of Glutaconic Acid. I. The Addition of Hydrogen Cyanide to Ethyl α -Cyano- β -methylglutaconate and its Homologues. EDWARD HOPE and WILFRID SHELTON (T., 1922, 121, 2223—2235).

Action of Uranyl Acetate on some Organic Substances. I. Action of Uranyl Acetate on Tartaric Acid and its Salts. FRITZ KOPATSCHEK (*Anal. Asoc. Quim. Argentina*, 1922, 10, 133—151).—An investigation of the effect of uranyl acetate on tartaric acid and tartrates, alone and in the presence of sugars, as shown by polarimetric determinations. Uranyl acetate combines with hydroxylic compounds but not with hydroxy-aldehydes. The compounds formed are optically active, the optical activity being

probably due to the formation of new asymmetric atoms or to the formation of new complex compounds of greater rotatory power. The formation of such compounds depends on the presence of one or more central hydroxyl groups. The reaction in the case of tartaric acid and tartrates is influenced by concentration. The use of uranyl acetate in the estimation of tartaric acid is suggested. The supposed compounds are sensitive to light and unstable.

G. W. R.

Keto-enolic Tautomerism. H. P. KAUFMANN (*Ber.*, 1922, 55, [B], 2255—2257).—A preliminary account of experiments with ethyl diacetylsuccinate (cf. Knorr and Kaufmann, this vol., i, 220), the details of which will be published subsequently.

The ferric chloride reaction is given only by the α -ester (dienol, m. p. 45°) and the $\alpha_2\beta$ -ester (semi-enol, m. p. 20°); the $\alpha_1\beta$ -ester (liquid semi-enol), on the other hand, does not give a coloration with ferric chloride when quite pure; the brown coloration previously attributed to it is due to the presence of small amounts of the isomeric $\alpha_2\beta$ -ester. It appears, therefore, that the ferric chloride reaction is not common to all enols.

The α - and $\alpha_2\beta$ -esters do not react with bromine under the conditions of K. H. Meyer's bromine titration method, which, however, may be applied to the $\alpha_1\beta$ -ester. It is, however, found that the direct and indirect methods lead to considerably different results. The cause of the discrepancy lies in the use of aqueous potassium iodide solution, since the presence of water causes secondary reactions which prevent the complete elimination of iodine. (The formation of ethyl diacetylfumarate by loss of hydrogen bromide from the additive compound primarily formed with bromine has been established.) The difficulty can be overcome by replacing the aqueous potassium iodide by a 10% solution of sodium iodide in alcohol, and this modification of the original process appears generally advisable.

The proportions of $\alpha_1\beta$ -, $\alpha_2\beta$ -, and β - and γ -esters in equilibrium in alcoholic solution has been determined by a combination of the bromine titration and colorimetric methods.

H. W.

The Addition of Ethyl Sodiocyanoacetate and Ethyl Sodio-malonate to Ethyl Muconate. ERNEST HAROLD FARMER (*T.*, 1922, 121, 2015—2022).

Determination of the Three Dissociation Constants of Citric Acid. A. BAIRD HASTINGS and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1922, 53, 269—276).—On the basis of the theoretical considerations previously outlined (this vol., i, 893), the three dissociation constants of citric acid have been calculated from the results of the electrometric titration of 0.1*M*-citric acid with *N*-sodium hydroxide. The values obtained are: $K'_1 = 8.3 \times 10^{-4}$, $K'_2 = 4.1 \times 10^{-5}$, $K'_3 = 3.2 \times 10^{-6}$.

E. S.

Decomposition of Aliphatic Ketones. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1922, [iv], 31, 863—867).—A continuation of the author's work (this vol., i, 803) on the behaviour of aliphatic ketones

when heated at 600° in presence of copper-aluminium. The substances here dealt with are methyl isopropyl ketone, methyl isobutyl ketone, methyl butyl ketone, methyl isoamyl ketone, diisopropyl ketone, isopropyl isobutyl ketone, and dihexyl ketone, and the results obtained show that decomposition readily occurs under the conditions of experiment with formation of products which are chiefly gaseous. The molecule is disrupted at the ketonic group with formation of carbon monoxide and liberation of the two residues. The latter react, by gain or loss of hydrogen, to yield either a saturated or an ethylenic hydrocarbon. When the residues are of a certain degree of complexity, they are further decomposed into simpler substances; this occurs with the butyl, isoamyl, isobutyl, and heavier groups. The composition of the gaseous products obtained varies with small increments of temperature, a rise of 20° to 30° being sufficient to bring about a marked change.

H. J. E.

Diacetylacetone. JOHN NORMAN COLLIE and AMY ADA BEATRICE REILLY (T., 1922, 121, 1984—1987).

Solubility of Dextrose in Water. R. F. JACKSON and CLARA G. SILSBEE (*U.S. Bureau of Standards, Sci. Papers*, 1922, No. 437, 715—724).—The equilibria in the system dextrose-water have been determined. At temperatures below 90°, three solid phases are capable of existence, namely, ice, α -dextrose monohydrate, and anhydrous α -dextrose. The freezing-point curve was computed from the data of Roth and of Abegg. The cryohydric point, determined graphically, lies at -5.3° (31.75% dextrose). The solid phase, α -dextrose monohydrate, which occurs in lustrous plates, is stable between -5.3° and 50° . Its solubility shows a very high temperature coefficient. Thus, at 0.5° , 100 parts of water dissolve 54.32 parts; at 50° , 243.76 parts of dextrose. The observed m. p., $80-90^\circ$, although located far from the extrapolated solubility curve, is shown to be compatible with the measurements, on the theory that β -dextrose is present in the saturated solution and absent during a m. p. determination. Above the transition point, 50° , the anhydrous form becomes stable. The solubility measurements of this phase in the metastable state were continued down to 28° .

CHEMICAL ABSTRACTS.

Carbohydrate-sulphates. IV. HEINZ OHLE (*Biochem. Z.*, 1922, 131, 601—610).—By the action of chlorosulphonic acid in chloroform at -10° on dextrose in pyridine and subsequent acetylation, the crystalline sodium salt of tetra-acetyldextrose- ζ -monosulphate is obtained. It has m. p. 137° (decomp.) and $[\alpha]_D +12.45^\circ$ in water. The pyridine salt has $[\alpha]_D +11.71^\circ$ and m. p. $158-160^\circ$. On hydrolysis with baryta, dextrose- ζ -monosulphate is isolated as the brucine salt, m. p. 184° , and $[\alpha]_D$ initially -4.07° , and after twelve hours -6.28° . Tetra-acetyldextrose on sulphonation gave the pyridine salt of tetra-acetyldextrose- α -monosulphate, m. p. 127° . $[\alpha]_D -4.65^\circ$ in water. The sodium salt has m. p. $149-151^\circ$ and $[\alpha]_D -6.23^\circ$ in water. By the action of silver sulphate on aceto-

bromoglucose in pyridine solution, a substance is obtained of doubtful constitution. It has m. p. 143—144° and $[\alpha]_D -13.99^\circ$ in chloroform, and loses the whole of its sulphur as sulphate instantly on treatment with baryta. The sodium salt of triacetyl β -methylglucoside-monosulphate has m. p. 141—142° and $[\alpha]_D -5.1^\circ$ in water, and on hydrolysis with baryta gave β -methylglucoside monosulphate. The brucine salt has m. p. 136—155° and $[\alpha]_D -32.5^\circ$ in water.

H. K.

The Constitution of Acetone Derivatives of Glucose and Fructose. JAMES COLQUHOUN IRVINE and JOCELYN PATTERSON (T., 1922, 121, 2146—2161).

γ -Methylfructoside. ROBERT CHARLES MENZIES (T., 1922, 121, 2238—2247).

Phosphoric Esters of some Substituted Glucoses and their Rate of Hydrolysis. P. A. LEVENE and G. M. MEYER [with I. WEBER] (*J. Biol. Chem.*, 1922, 53, 431—435).—In previous papers on this subject (A., 1920, i, 712; 1921, i, 845), incorrect positions were assigned to certain groups in two of the esters. The substances described as phosphoric ester of ζ -benzoyl- $\alpha\beta$ -monoacetoneglucose and ζ -phosphoric esters of α -, β -, γ -, ϵ -diacetoneglucose were, in reality, the ϵ - or ζ -phosphoric ester of γ -benzoyl- $\alpha\beta$ -acetoneglucose and the γ -phosphoric esters of α -, β -, ϵ -, ζ -diacetoneglucose, respectively. When these corrections are made, it appears that the more resistant esters are those with the phosphoric acid group in the ϵ - or ζ - (probably the latter) position. Benzylidene-monoacetone glucose, m. p. 141—142°, $[\alpha]_D^{25} +22^\circ$, was prepared from monoacetoneglucose. With phosphoryl chloride, it gave the ζ -phosphoric ester of $\alpha\beta$ -monoacetoneglucose, isolated in the form of its amorphous barium salt. The hydrolysis constant of this was 17×10^{-3} . The abnormal results previously obtained with the β -phosphoric ester of $\gamma\epsilon\zeta$ -trimethyl methyl glucoside are now attributed to admixture with the ζ -phosphoric ester of $\beta\gamma\epsilon$ -trimethyl methyl glucoside.

E. S.

Sulphuric Esters of some Substituted Glucoses and their Rates of Hydrolysis. P. A. LEVENE and G. M. MEYER [with I. WEBER] (*J. Biol. Chem.*, 1922, 53, 437—440).—The γ -sulphuric ester of α -, β -, ϵ -, ζ -diacetoneglucose, isolated in the form of its amorphous barium salt, was obtained by the action of sulphuryl chloride on diacetoneglucose. The ϵ - or ζ -sulphuric ester of $\alpha\beta$ -monoacetoneglucose was similarly obtained from γ -benzoyl $\alpha\beta$ -monoacetoneglucose. These substances gave hydrolysis constants of 60×10^{-3} and 40×10^{-3} , respectively.

E. S.

Methylation of Xylose. ALBERT CARRUTHERS and EDMUND LANGLEY HIRST (T., 1922, 121, 2299—2308).

A New Depolymerisation Product of Starch. AMÉ PICTET and R. JAHN (*Helv. Chim. Acta*, 1922, 5, 640—644).—By heating potato starch in glycerol at 200—210°, distilling off the glycerol

under reduced pressure at the same temperature, and purifying the residue by dissolving in water and precipitating by means of alcohol, a new decomposition product of starch was obtained having the formula $(C_6H_{10}O_5)_3$. It forms a white, amorphous, slightly hygroscopic powder, $[\alpha]_D$ in water $+162.2^\circ$. It does not give a coloration with iodine, and is identical neither with Pringsheim's triamylose or isotriamylose (A., 1913, i, 1156) nor with Karrer's β -hexamylose (this vol., i, 435), which may be identical with triamylose. It does not reduce Fehling's solution at the boiling temperature, and when hydrolysed with hot dilute sulphuric acid gives dextrose. It forms a *nona-acetyl* derivative, $[C_6H_7O_5(Ac)_3]_3$, m. p. $153-154^\circ$. The name *trihexosan* is proposed provisionally. The existence of the compound confirms the presence in the starch molecule of $C_6H_{10}O_5$ units combined in groups of three, and cannot be reconciled with the idea that starch is a polymeride of an anhydride of maltose. E. H. R.

Preparation and Properties of Cellulose Solutions. P. WAENTIG (*Papierfabr.*, 1922, 20, 359-361; from *Chem. Zentr.*, 1922, ii, 1063-1064).—Viscose solutions, suitably prepared, do not change so quickly as copper solutions. Cellulose, artificially prepared, is very sensitive to time, temperature, and method of bleaching, and to treatment with acids and alkalis. Heating with dilute alkaline solutions increases the viscosity of viscose solution. The changes in viscosity are conditioned by colloidal as well as by chemical changes. It may be assumed that there is a difference in constitution between cotton and artificial cellulose, the latter probably consisting of molecular aggregates of differing sizes. Treatment with boiling dilute alkaline solutions results in a simplification of larger aggregates and a solution of smaller aggregates. G. W. R.

Reactions of Cellulose with Sodium Chloride and other Neutral Salt Solutions. I. Preliminary Survey. HELEN MASTERS (T., 1922, 121, 2026-2034).

Cellulose. VII. Cellulose Copper Compounds. KURT HESS and ERNST MESSMER [in part with FR. E. JAGLA] (*Ber.*, 1922, 55, [B], 2432-2443).—It has been pointed out previously (A., 1921, i, 401) that the enhanced specific rotation of cellulose in ammoniacal copper hydroxide solutions is probably due to the formation of a complex copper compound. Measurements are now recorded of the specific rotations of such solutions with increasing concentration of copper and constant concentration of cellulose, and conversely with increasing cellulose and constant copper content. The concentration of ammonia, which within wide limits does not affect the specific rotation appreciably, was kept uniform throughout. The results, particularly in the case of the first series of measurements, are in harmony with the hypothesis of the union of the molecules $C_{12}H_{20}O_{10}$ and $Cu(OH)_2$. Similar experiments are recorded with the biose anhydride, obtained from cellulose by means of acetyl chloride and hydrogen chloride, which

in Schweizer's reagent has a specific rotation of the same order as cellulose. Apparently, on account of dissociation, the results are not easy to interpret; this suggestion is supported by the observed influence of sodium hydroxide on the specific rotation of the solutions.*

Indications of the nature of the copper complex are found in the observation that the blue zone wanders towards the anode when a solution of the biose anhydride in Schweizer's reagent is subjected to electrolysis in the presence of sodium hydroxide, whereas, in the absence of the latter the copper wanders towards the cathode. Cathodic copper thus appears to be displaced into the anion by sodium hydroxide (similar results are recorded with solutions of glycerol and mannitol), and, in addition, the dissociation of the sodium copper salt is depressed by the excess of alkali. This is in complete harmony with the observation that a copper-biose anhydride solution gives a *precipitate* when treated with an excess of sodium hydroxide which contains copper, sodium, and carbon in the atomic ratio 1 : 2 : 12.

Similar experiments with cellulose show that the specific rotations of solutions of the latter in Schweizer's reagent are increased in a similar manner by the addition of sodium hydroxide, that copper is displaced from the kation to anion by the addition of the alkali, and that a compound containing copper, sodium, and carbon in the atomic ratio 1 : 2 : 12 is also formed.

The capacity of the biose anhydride for combining with copper in solution is not exhausted when the substances are present in the proportion $1\text{Cu} : 1\text{C}_{12}\text{H}_{20}\text{O}_{10}$.

H. W.

The Reduction of Lignin and of Carbohydrates with Hydrogen Iodide and Phosphorus. R. WILLSTÄTTER and L. KALB (*Ber.*, 1922, 55, [B], 2637—2652).—The behaviour of lignin towards hydrogen iodide and phosphorus is so closely similar to that of carbohydrates that the substances must be considered as nearly related in constitution. The formulae for lignin proposed by Cross and Bevan and subsequently by Klason, which involve a relationship to aromatic substances, appear therefore to be improbable, whereas the authors' views in their more important features coincide with those of Fuchs (*A.*, 1921, i, 309) and Jonas (*A.*, 1921, ii, 554).

The lignin is obtained from pine and red beech, respectively, by treatment with hydrochloric acid (d 1.21), in accordance with the method of Willstätter and Zechmeister (*A.*, 1913, i, 955). It is converted by boiling hydriodic acid (d 1.96) and red phosphorus into a granular product which contains iodine; dehalogenation can only be effected incompletely with zinc dust in boiling glacial acetic acid solution. The final material is a pale grey or yellow resin; it is not homogeneous, and appears to consist mainly of two substances of faintly acidic character. A more promising material is obtained by treating lignin under pressure at about 250° with red phosphorus and hydriodic acid (d 1.7); the products from pine and red beech lignins resemble one another closely, but

differ in the relative quantities of their constituents. The portion of the product which does not dissolve in ether is a pale grey, non-homogeneous mass, which melts at a very high temperature with decomposition and distillation of difficultly-volatile oils. The portion which dissolves in ether is separated by treatment with alkali into an acidic material (C=76.50%, H=10.39%), an almost colourless, brittle resin, and a mixture of hydrocarbons. The latter is separated by successive treatment with acetone and glacial acetic acid into a solid and a liquid portion both of which are free from oxygen. The composition of the mixture approximates to a mean value which corresponds with the formula C_7H_{14} ; the liquid portion is somewhat richer, the solid portion somewhat poorer in hydrogen. The liquid hydrocarbons have d 0.9–1.0 for the fractions of lowest and highest boiling point. The lowest observed molecular weight is 167, the highest 842 (for the solid portion). The two mixtures are an interrelated analogous (not homologous) series the properties of which are reminiscent of that of hydroaromatic hydrocarbons.

The four different fractions thus obtained have been separately subjected to further treatment with hydriodic acid and phosphorus. The purified residue, which is insoluble in ether, is almost completely converted into the mixture of solid hydrocarbons. The acid substance yields mainly solid together with some liquid hydrocarbons, the approximate ratio being 3 : 1. The liquid and solid hydrocarbon mixtures are practically unaffected.

[With G. von MILLER.]—Hexitol, dextrose, xylose, and cellulose yield mixtures similar to those derived from lignin when treated with hydriodic acid and phosphorus under exactly similar conditions. The analogy extends to the production of the feebly acidic material and a product which is insoluble in all media. Xylose and cellulose yield larger proportions of compounds of high molecular weight than do dextrose and hexitol. These are also obtained in quantity from the humus-like material prepared by treating dextrose with hydrochloric acid. The known convertibility of hexitol into *n*-hexyl iodide suggests the possibility that the haloid is an intermediate product in the change; this cannot, however, be the case, since it does not give a mixture of hydrocarbons under the experimental conditions actually used. It appears more probable that the intermediate compound is a derivative of furan or a di-olefine.

H. W.

Catalytic Synthesis of Hexamethylenetetramine. LAWRENCE E. ROMBAULT and JULIUS A. NIEUWLAND (*J. Amer. Chem. Soc.*, 1922, **44**, 2061).—Hexamethylenetetramine is formed in small amount when a mixture of carbon monoxide, hydrogen, and ammonia at the atmospheric pressure is passed over a mixture of equal parts of reduced, finely-divided nickel and very pure diatomaceous earth heated to 250–280°. A trace of ammonium cyanide and a relatively large quantity of ammonium carbonate are also produced, the latter undoubtedly resulting from the reaction, $2\text{CO} \rightarrow \text{C} + \text{CO}_2$, since a deposition of carbon is noticed

in the reaction chamber. Reaction does not occur when the nickel catalyst is replaced by platinised asbestos. The effectiveness of a catalyst in this synthesis undoubtedly depends on its ability to form an unstable carbonyl.

H. W.

Preparation of Hexamethylenetetramine Derivatives.

J. D. RIEDEL, AKT.-GES (D.R.-P. 346383; from *Chem. Zentr.*, 1922, ii, 1081).—Ethylene halogenhydrins are allowed to act, with or without solvents, on hexamethylenetetramine. The additive compound of hexamethylenetetramine and ethylene chlorohydrin forms crystals, m. p. 135° (decomp.). The additive compound of hexamethylenetetramine with ethylene iodohydrin forms rod-like prisms, m. p. 149° (decomp.).

G. W. R.

Preparation of Additive Products of Hexamethylenetetramine with Esters of Monohalogen Fatty Acids.

J. D. RIEDEL, AKT.-GES (D.R.-P. 346462; from *Chem. Zentr.*, 1922, ii, 1081; cf. A., 1921, i, 774).—Hexamethylenetetramine is allowed to act on monobromoacetic esters of alcohols or phenols which are insoluble or slightly soluble in water. The additive compound of bornyl bromoacetate and hexamethylenetetramine is a white, crystalline powder from which borneol separates gradually on warming with water. The additive compound of thymyl bromoacetate (from thymol, bromoacetic acid, and phosphoryl chloride, a yellow, heavy oil, b. p. 153–157°/4 mm.) and hexamethylenetetramine forms colourless needles, m. p. 155–157°. Thymol is liberated on warming the aqueous solution. At body temperature, these compounds break up into the alcohol or phenol and the antiseptic additive compound of bromoacetic acid and hexamethylenetetramine.

G. W. R.

Preparation of Amino-alcohols. PAUL KARRER (D.R.-P. 347377; from *Chem. Zentr.*, 1922, ii, 1137–1138).—Ethyl α -acetyl-amino- γ -methylvalerate, $\text{CHMe}_2\text{CH}_2\text{CH}(\text{NHAc})\text{CO}_2\text{Et}$, mixed with ethyl alcohol, is allowed to act on metallic sodium with occasional heating. After heating for two to three hours and adding ethyl alcohol, water is added and the alcohol distilled off. On extraction with ether, β -amino- δ -methylamyl alcohol, $\text{CHMe}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$, is obtained as a colourless oil of basic odour, b. p. 194°. It forms crystalline salts with acids, for example, the hydrosulphate or hydrochloride, m. p. 148–150°. An optically active (lævorotatory) β -amino- δ -methylamyl alcohol may be obtained by starting from optically active leucine. β -Amino- γ -phenylpropyl alcohol, $\text{CH}_2\text{PhCH}(\text{NH}_2)\text{CH}_2\text{OH}$, prepared from the ethyl ester of acetylphenylalanine, is a viscid oil with basic odour having b. p. 150–160° in a vacuum. It forms crystalline salts with acids; the hydrochloride has m. p. 128°. By acetylation of the products of hydrolysis of casein and subsequent reduction with sodium and ethyl alcohol, a mixture of amino-alcohols is obtained having b. p. 50–240°/16 mm. By fractionation, the following may be obtained. Up to 175°/16 mm., colamine, alaninol, etc.; 105–190° [? 175–190°]/16 mm., valine alcohol, leucine

alcohol, phenylalanine alcohol; and a fraction distilling over at 190—235°/16 mm. The products have therapeutic uses and serve as intermediate products.

G. W. R.

Preparation of Cystine. CARL L. A. SCHMIDT (*Proc. soc. exp. biol. med.*, 1921, **19**, 50—52; from *Chem. Zentr.*, 1922, i, 1277).—Human hair, or wool, from which fat has been extracted, is hydrolysed with twice its weight of concentrated hydrochloric acid until the biuret reaction has almost or completely disappeared. This takes place in approximately twelve hours, longer heating being undesirable. The greater part of the liquid is then distilled off in a vacuum at 60—70°. Water is added up to the original volume and a thick suspension of calcium hydroxide is added, avoiding rise in temperature, until a chocolate-brown colour is obtained. After filtering and washing with water, the filtrate, which should be clear and of light brown colour, is partly neutralised with hydrochloric acid and finally acidified with acetic acid. On keeping in an ice-chest, cystine separates. It is purified by dissolving in the least possible quantity of 5% hydrochloric acid, decolorising with animal charcoal, and again precipitating by the addition of sodium acetate until the liquid is no longer acid to congo-red. After filtering and washing with water until tyrosine is completely removed, a yield of cystine amounting to 6.3% is obtained.

G. W. R.

Preparation of Carbamide. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 301279; Brit. Pat. 145060; from *Chem. Zentr.*, 1922, ii, 1135—1136).—Carbon dioxide and ammonia are heated together under pressure and the product is maintained at the necessary temperature sufficiently long for the ammonium carbamate to be changed into carbamide (for example, two hours at 135°). The mixture of carbon dioxide and ammonia disengaged on removal of the product from the autoclave is again led back into the autoclave under pressure, whilst the carbamide is obtained free from ammonium salts.

G. W. R.

The Constitution of Carbamides. XIV. The Decomposition of Urea by Sodium Hypobromite in Alkaline Solution, and an Improved Procedure for the Estimation of Urea by this Means. EMIL ALPHONSE WERNER (T., 1922, **121**, 2318—2325).

Preparation of Bromodialkylacetylcarbamides. FARBEY-FABRIKEN VORM. FRIEDRICH BAYER & CO. (D.R.-P. 347609; Swiss Pat. 92296; from *Chem. Zentr.*, 1922, ii, 1111—1112).—Dialkylmalonic acids of the general formula $\text{CO}_2\text{H}\cdot\text{CR}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ (R=alkyl) are treated with bromine with or without addition of solvents, or diluents, or bromine carriers. The reaction proceeds at 100° with elimination of carbon dioxide. For example, diethylmalonic acid is heated with an equal weight of bromine and some aluminium chloride at 100° under a reflux apparatus until the evolution of hydrogen bromide and carbon dioxide is completed.

From the residue, *bromo- α -ethylbutylcarbamide*, m. p. 118—120°, is obtained with 80—85% of the theoretical yield. G. W. R.

Preparation of Carbamide from Cyanamide. FAREWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.P. 301278; from *Chem. Zentr.*, 1922, ii, 1135).—Cyanamide is warmed in acid solution with the sediment, consisting of ferrosiferrous oxide, obtained from the reduction of nitro-compounds by iron. For example, cyanamide solution acidified with sulphuric acid is warmed at 80° and a paste containing 83% of ferrosiferrous oxide is added with shaking. The transformation to carbamide is complete in one hour. In acid solution no dicyandiamide is formed; neither, in dilute solution, does the cyanamide combine with the sulphuric acid. A smaller amount of catalyst is needed than where ferric oxide or ferric hydroxide is used. G. W. R.

Quantitative Reduction by Hydriodic Acid of Halogenated Malonyl Derivatives. II. The *s*-Tetra-substituted Amides of Bromo- and Chloro-malonic Acid. RALPH WINTON WEST (T., 1922, 121, 2196—2202).

The Oxime of Mesoxamide (isoNitrosomalonomamide) and some Allied Compounds. IV. The Ethers of isoNitrosomalonanilide, isoNitrosomalondimethylamide, and isoNitrosomalondibenzylamide. ARTHUR GEOFFREY RENDALL and MARTHA ANNIE WHITELEY (T., 1922, 121, 2110—2119).

Iron as Photochemical Catalyst. I. The Decomposition of Potassium Ferrocyanide in Daylight. OSKAR BAUDISCH and LAWRENCE W. BASS (*Ber.*, 1922, 55, [B], 2698—2706).—A pale yellow, alkaline solution of potassium ferrocyanide in water speedily becomes lemon-yellow in colour when exposed to direct sunlight in the complete absence of oxygen, but reverts to its original tint when placed in the dark. After some time, colourless crystals of ferrous hydroxide separate in very small amount; these do not redissolve when the mixture is removed from the light. The change in colour is not therefore due to the formation of a peroxo-compound as supposed previously (A., 1921, ii, 337). In the presence of air, the initial intensely yellow coloration is succeeded by a brown turbidity and ultimate separation of ferric hydroxide. The first part of the change in the absence of air is accompanied by a reversible development of alkalinity in the solution and at this stage the presence of active oxygen (which is formed later) cannot be detected. The two processes are considered to occur

in accordance with the schemes (I)
$$\left[\text{Fe} \begin{smallmatrix} \text{NC} \\ \text{NC} \end{smallmatrix} \right] \text{K} \xrightarrow{+\text{TiO}_2 + \text{light}} \left[\text{Fe} \begin{smallmatrix} \text{NC} \cdot \text{H} \\ \text{NC} \end{smallmatrix} \right] \text{K} \cdot \text{OH} \quad \text{and} \quad \text{(II)} \quad \left[\text{Fe} \begin{smallmatrix} \text{NCH} \\ \text{NC} \end{smallmatrix} \right] \text{K} \xrightarrow{\text{H}_2\text{O}} \left[\text{Fe} \begin{smallmatrix} \text{OH}_2 \\ \text{NC} \end{smallmatrix} \right] \text{K} + \text{HCN} + \text{KOH}.$$
 Confirmation of this hypothesis is found in the observation that an intensely blue colour is developed when nearly colourless, oxygen-free solutions of potassium ferrocyanide and nitrosobenzene are exposed in a vacuum to sunlight, $[\text{Fe}(\text{NC})_5]\text{K}_4 +$

$\text{PhNO} \xrightarrow{\text{light}} \left[\text{Fe} \begin{smallmatrix} \text{Ph}\cdot\text{NO} \\ (\text{CN})_5 \end{smallmatrix} \right] \text{K}_3 + \text{KCN}$. The primary production of a pentacyano-compound is also established by the formation of potassium pentacyanoperoxoferroate, $\left[\text{Fe} \begin{smallmatrix} \text{O}_2 \\ (\text{NC})_5 \end{smallmatrix} \right] \text{K}_3$. The subsequent photochemical decomposition of the pentacyano-compound has not been studied in detail, but appears to proceed in a somewhat complex manner since sodium pentacyanoaquoferroate in almost complete absence of oxygen is rapidly and completely converted by light energy into ionised substances. Freshly prepared aqueous solutions of sodium pentacyanoaquoferroate are alkaline in reaction and contain active oxygen shortly after their exposure to the air, even in the absence of light.

The experiments just described have caused the author to modify his views somewhat as to the nature of ferrous hydroxide peroxide which is now formulated, $\left[\text{Fe} \begin{smallmatrix} \text{O}_2\text{H} \\ (\text{OH}_2)_5 \end{smallmatrix} \right] (\text{OH})_2$; the group, O_2H , co-ordinately united to the iron ion is able to decompose into O_2 and H , that is, active molecular oxygen and atomic hydrogen, thus explaining its simultaneous behaviour as oxidising and reducing agent. H. W.

Mechanism of Reaction of Aliphatic Diazo-compounds. E. OLIVERI-MANDALÀ (*Gazzetta*, 1922, 52, ii, 103—111).—The author discusses the formation of heterocyclic rings by the addition of diazo-derivatives of aliphatic hydrocarbons to unsaturated compounds, and the reaction of these diazo-derivatives with compounds of even slight acid properties, $\text{RH} + \text{CH}_2\text{N}_2 = \text{CH}_3\text{R} + \text{N}_2$. These two reactions are regarded as essentially similar in character, and the conclusion is drawn that diazo-hydrocarbons are capable of causing intramolecular transformations as a result of processes of addition and elimination occurring at unsaturated linkings. It is, therefore, not considered possible to draw accurate conclusions concerning the structures of compounds from those of the alkyl derivatives obtained on etherification by means of diazo-derivatives of aliphatic hydrocarbons. T. H. P.

Organic Compounds of Arsenic. VIII. Action of Cyanogen Bromide on Tertiary Arsines. WILHELM STEINKOPF, HANS DONAT, and PAUL JAEGER (*Ber.*, 1922, 55, [B], 2597—2614; cf. this vol., i, 118, and previous abstracts).—In contrast to tertiary amines, tertiary arsines, even when they contain two or three phenyl groups, combine with cyanogen bromide to form arsine bromocyanides which are readily hydrolysed but otherwise are relatively stable and suffer fission only at an elevated temperature. Triphenylarsine bromocyanide is decomposed thereby mainly into its components. All bromocyanides of aliphatic or aliphatic-aromatic substituted arsines lose alkyl bromide and give cacodyl cyanides. Loss of methyl precedes that of ethyl, *n*-propyl, or phenyl, that of ethyl takes place before *isobutyl* and phenyl, whereas elimination of ethyl and *n*-propyl occurs with about equal

readiness. The firmness of the attachment of hydrocarbon residues to arsenic and to carbon is therefore not the same, at any rate as far as the unsymmetrical pinacones are concerned (cf. Meerwein, A., 1920, i, 2). *cyclopentamethylarsine* derivatives yield bromocyanides which decompose in a complex manner, without, however, giving evidence of the rupture of the arsenic ring such as is evidenced by *N*-phenylpiperidine; the *cyclopentamethylene-arsenic* ring is therefore more stable towards cyanogen bromide than the piperidine ring. The greater stability of the bromocyanides of the arsines as compared with the amines depends on the more metallic and positive character of the arsenic atom. The introduction of strongly negative groups into the molecule of the arsine (trinitrotriphenylarsine) deprives the latter of its ability to unite with cyanogen bromide.

Diphenylethylarsine, AsPh_2Et , b. p. 162–163°/10 mm., prepared by the action of magnesium ethyl bromide on diphenylchloroarsine in ethereal solution, is converted by cyanogen bromide in the presence of light petroleum into *diphenylethylarsine bromocyanide*, $\text{AsPh}_2\text{EtBr}\cdot\text{CN}$, m. p. 75°, which is decomposed when heated into ethyl bromide and *diphenylcyanarsine*, b. p. 207–209°/23 mm., m. p. 31.5°. *Diphenylethylarsine hydroxybromide*, m. p. 97.5°, is prepared from diphenylethylarsine and cyanogen bromide in ethereal solution; the corresponding *picrate*, $\text{AsPh}_2\text{Et}(\text{OH})\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_3$, crystallises in lemon-yellow leaflets, m. p. 116°.

Ethyl-di-n-propylarsine, a highly refractive liquid, b. p. 60–64°/14 mm., prepared from ethyldichloroarsine and magnesium *n*-propyl bromide in ethereal solution, gives *ethyl-di-n-propylarsine bromocyanide*, a granular substance which is unusually sensitive towards moisture. It is decomposed by heat into a mixture of ethyl bromide (about 25%) and propyl bromide (about 75%) and of *ethyl-n-propylcyanoarsine* and *di-n-propylcyanoarsine* (a little of the original material remains undecomposed and is identified as *methylethyl-di-n-propylarsonium iodide*, m. p. 175°). *Ethyl-di-n-propylarsine hydroxybromide* is too hygroscopic to permit of its isolation, but its formation (in the manner described for the corresponding diphenylethyl compound) is established by the isolation of the corresponding *picrate*, a yellow, crystalline powder, m. p. 85.5°.

Ethyl-diisobutylarsine, from ethyldichloroarsine and magnesium isobutyl bromide, is a colourless, highly refractive liquid, b. p. 86°/16 mm., which is transformed in the usual manner into *ethyl-diisobutylarsine bromocyanide*, m. p. 69°, and *ethyl-diisobutylarsine hydroxy-bromide*, which could not be caused to crystallise (the corresponding *hydroxy-picrate* crystallises in slender, yellow needles, m. p. 82°). The bromocyanide is decomposed by heat into ethyl bromide and *diisobutylcyanoarsine*, b. p. 116°/16 mm. *Phenyl-methylethylarsine*, b. p. 93–99°/11 mm., prepared from phenyl-methylchloroarsine and magnesium ethyl bromide, gives *phenyl-methylethylarsine bromocyanide*, which could not be caused to

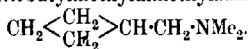
solidify, and *phenylmethylethylarsine hydroxy-bromide*, a colourless, microcrystalline mass, m. p. 83° (*hydroxy-picrate*, a pale yellow, crystalline powder, m. p. 113.5°). Fission of the cyanide gives rise to methyl bromide and *phenylethylcyanoarsine*, a colourless liquid, b. p. 148—150°/23 mm. *Phenylmethyl-n-propylarsine*, a colourless liquid, b. p. 105—106°/12 mm., prepared from phenylmethylchloroarsine and magnesium *n*-propyl bromide, gives a non-crystalline bromocyanide, and *phenylmethyl-n-propylarsine hydroxy-bromide*, m. p. 146° (corresponding *hydroxy-picrate*, brilliant yellow needles, m. p. 84°). The bromocyanide is decomposed by heat into methyl bromide and *phenyl-n-propylcyanoarsine*, b. p. 150—155°/20 mm.

Phenylbenzylmethylarsine, b. p. 174—177°, is prepared from phenylmethylchloroarsine and magnesium benzyl bromide. The corresponding bromocyanide could not be isolated in a homogeneous condition, but its existence is established by converting it into *phenylbenzylmethylarsine hydroxy-bromide*, a microcrystalline powder, m. p. 147° (*hydroxy-picrate*, yellow needles, m. p. 119°).

Ethylcyclopentamethylenearsine, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{AsEt}$, b. p. 62—64°/12.5 mm., is obtained in poor yield by the addition of an ethereal solution of ethyldichloroarsine to a well-stirred ethereal solution of the Grignard reagent from α -dibromopentane. It is readily converted by methyl and ethyl iodide into *methylethylcyclopentamethylenearsonium iodide*, a somewhat unstable solid, m. p. 276°, and *diethylcyclopentamethylenearsonium iodide*, respectively. *Ethylcyclopentamethylenearsine bromocyanide* is extremely sensitive to moisture; *ethylcyclopentamethylenearsine hydroxy-bromide* has m. p. 71°. The decomposition of the bromocyanide by heat proceeds in a somewhat complicated manner, giving as identifiable products *ethylcyclopentamethylenearsine* (identified as the methiodide, m. p. 276°), cyanogen bromide, and ethyl bromide.

Trinitrotriphenylarsine does not appear to react with an excess of cyanogen bromide at 55°. H. W.

Methylenecyclobutane and Dimethylcyclobutylmethylamine. N. J. DEMJANOV and MARIE DOJARENKO (*Ber.*, 1922, 55, [B], 2727—2730).—Unsuccessful attempts are recorded to prepare methylenecyclobutane, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{CH}_2$, by the action of heat on cyclobutylmethylamine nitrite, of oxalic acid on cyclobutylmethyl alcohol, or by the distillation of cyclobutylmethylamine phosphate; in every case isomerisation to cyclopentene occurred. The desired compound has, however, been obtained by the application of Hofmann's reaction to cyclobutylmethyltrimethylammonium hydroxide, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{NMe}_3 \cdot \text{OH}$; the yield of the hydrocarbon is small, since the base is mainly decomposed into cyclobutylmethyldimethylamine,



Methylenecyclobutane has b. p. 40.6—41.6°/32 mm., d_4^{20} 0.7585, n_D^{20} 0.7487, d_4^{25} 0.7425, n_D^{25} 1.42626, n_D^{25} 1.42353; its identity with Gustavson's "vinyltrimethylene" is established by its physical properties and comparison of the nitrosites from either source.

cycloButylmethyldimethylamine has b. p. 125.4—126°/740 mm., d_4^{20} 0.8143, d_4^{25} 0.8056, d_4^{25} 0.8019, n_D^{20} 1.4356, n_D^{20} 1.43408. The corresponding hydrochloride, long prisms; platinichloride, long, lustrous prisms; aurichloride, large, yellow crystals; picrate, long, yellow prisms, m. p. (indefinite) 130°, and methiodide, large, pale yellow crystals, are described.

H. W.

The Structure of Benzene. MAURICE I. HUGGINS (*Science*, 1922, **55**, 679—680).—A theory of conjugation similar to that of Erlenmeyer (*Annalen*, 1901, **316**, 43, 71, 75) has been developed, and found to be subject to one objection only, namely, that ortho- and meta-disubstitution products should give stereoisomerides. In this model, the six carbon tetrahedra have their bases all in the same plane, the hydrogen atoms and the points of the tetrahedra to which they are bonded being alternately above and below this plane. There are six electrons grouped round the centre of each hexagon, and two at each of the hexagon corners and on the centre lines between each hydrogen atom and the carbon atom to which it is bonded. The structure of graphite, as determined by X-ray analysis (Debye and Scherrer, *Physikal. Z.*, 1916, **17**, 277; A., 1917, ii, 437; Hull, *Physical Rev.*, 1917, **10**, 661; Anon, *Engineering*, 1917, **104**, 594), is exactly that which would be obtained if it were built up of layers of benzene hexagons of the type described, the carbon-hydrogen bonds of the benzene molecules being replaced by carbon-carbon bonds between the layers. In the case of a considerable number of aromatic compounds in which large distortions would not be expected, the dimensions of the hexagon are very close to the corresponding dimensions in graphite.

A. A. E.

Monochlorotrinitrobenzenes. A. F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 223—224).—Of the six possible isomeric monochlorotrinitrobenzenes, picryl chloride and 1-chloro-3 : 4 : 6-trinitrobenzene alone have hitherto been prepared. The author describes the preparation of three of the missing isomerides. 1-Chloro-3 : 4 : 5-trinitrobenzene is prepared by substituting the nitro-groups of 4-chloro-3 : 5-dinitroaniline by amino-groups by Körner and Contardi's method. The product crystallises in large, yellow crystals, m. p. 168°, in a 70% yield. On treating 1-chloro-2 : 3-dinitrobenzene with a mixture of fuming nitric acid and 50% oleum at 160—170° for five hours and pouring the product into water, an oil is obtained which after some time partly crystallises. The crystals are separated by centrifuging and recrystallised from alcohol, and shown to be 1-chloro-2 : 3 : 5-trinitrobenzene, m. p. 166°, by conversion into 2-chloro-4 : 6-dinitroaniline, m. p. 159°, which is well known. On keeping the mother-liquor from the nitration above, other crystals separate after a long time and

these are found to be 1-chloro-2:3:4-trinitrobenzene, m. p. 69°. A better method of preparing 1-chloro-3:4:6-trinitrobenzene than that described by Nietzki is described, which consists in passing ammonia into an alcoholic solution of 1:3-dichloro-4:6-dinitrobenzene until a test portion has the melting point of 3-chloro-4:6-dinitroaniline (174°). The amino-group is then replaced by the nitro-group by Körner and Contardi's method. J. F. S.

Oxidation of Side-chains with Potassium Permanganate.

II. LUCIUS A. BIGELOW (*J. Amer. Chem. Soc.*, 1922, **44**, 2010—2019).—In a previous communication (A., 1920, i, 20) the behaviour of the three nitrotoluenes towards potassium permanganate has been described; the work has now been extended to the three bromotoluenes.

The oxidations are effected in a copper vessel provided with a reflux condenser and an efficient stirrer. The bromotoluene is heated with the requisite amount of sodium hydroxide solution almost to boiling, the potassium permanganate is added in one portion and gentle ebullition and vigorous agitation are maintained until the pink colour of the permanganate disappears.

Nearly all the influences which have been brought to bear on the oxidations are found to have a considerable effect on the reactions, but the result in every case is merely to alter the proportion of bromotoluene attacked by the permanganate, the sum of the bromobenzoic acid and unchanged bromotoluene remaining essentially constant. The same observation has been recorded with the nitrotoluenes. This emphasises the conclusions that the quantity of organic matter entirely destroyed during the reaction is practically independent of variations in procedure, and that two entirely independent changes occur within the reacting mixture, (a) the oxidation of the side-chain to carboxyl, and (b) the decomposition of the permanganate into oxides of manganese and free oxygen; differing conditions merely accelerate the one or the other of these changes, causing varying amounts of material to be attacked before all the permanganate has been destroyed.

An increasing concentration of alkali in the oxidation mixture, beyond a certain very low concentration, retards the oxidation of all three bromotoluenes, but, in the case of the meta-isomeride this effect is not observed until the alkaline strength of the solution becomes very considerable. The absence of accelerating action of the alkali hydroxide is attributed to the impossibility of any of the bromotoluenes passing into a quinoid form (cf. A., 1920, i, 20).

The effect of using an excess of potassium permanganate above that required theoretically for the oxidation of the bromotoluene is peculiar. In general, the reaction is favoured, except perhaps when the oxidising agent is present in great excess. In the cases of the ortho- and meta-derivatives the effect is not quite uniform, the oxidation being favoured, retarded, and favoured again as the excess of permanganate is increased. It does not appear at present possible to explain these peculiarities.

As in the case of the nitrotoluenes, increasing dilution of the

reaction mixture favours the oxidation of the bromotoluenes. This is doubtless due to the fact that alkaline permanganate solutions have a decreasing tendency to dissociate into free oxygen and manganate as they become more dilute.

The rate of reaction is approximately the same in the oxidation of the three bromotoluenes, although slightly greater with the para-compound than with the other isomerides. It is less than with the nitrotoluenes. It is not greatly affected by changes in the alkalinity of the reaction mixture. *p*-Bromotoluene gives the highest yield of the corresponding acid; the meta-isomeride gives the next highest yield, and the ortho-derivative the lowest.

Improved methods are described in detail for the preparation of *o*-bromotoluene from *o*-toluidine, of *m*-bromotoluene from *m*-bromo-*p*-toluidine, and of *p*-bromotoluene from *p*-toluidine.

H. W.

Preparation of Mono-substituted Sulphonamides. FARBEN-FABRIKEN VORM. FRIEDRICH BAYER & CO. (D.R.-P. 346810; from *Chem. Zentr.*, 1922, ii, 1136—1137).—Sulphonamides are treated with alkylating or arylalkylating reagents in the presence of carbonates. Mono-substituted derivatives of the composition $\text{R}\cdot\text{SO}_2\cdot\text{NHR}'$ are obtained without the formation of disubstitution products. *p*-Toluene-*p*-sulphonethylamide is obtained by heating toluene-*p*-sulphonamide with sodium ethyl sulphate and sodium carbonate at 170—200°. *p*-Toluene-*p*-sulphonbenzylamide, m. p. 115—117°, is similarly prepared by the action of benzyl chloride on toluene-*p*-sulphonamide in the presence of sodium carbonate or calcium carbonate.

G. W. R.

Investigations and Ring Closures in the Methylnaphthalene Series. FRITZ MAYER AND ADOLF SIEGLITZ (*Ber.*, 1922, 55, [B], 2940).—An addendum to a previous communication (this vol., i, 740).

Naphthalene-1 : 4-dicarboxylic acid has been described previously by Scholl and Neumann (this vol., i, 261); it has m. p. 309° instead of 288° as previously given. 4-Benzoyl-1-methylnaphthalene can also be prepared from α -methylnaphthalene and benzoyl chloride; it melts at 74—75° (instead of 174—175°). 4-Methylperibenzanthrone has m. p. 193—194° (instead of 115°). The boiling point of 1-benzoyl-2-methylnaphthalene is 140—145°/15 mm. (instead of 240—245°).

H. W.

2 : 6-Dimethylnaphthalene. FRITZ MAYER AND ERIKA ALKEN (*Ber.*, 1922, 55, [B], 2278—2285).—2 : 6-Dimethylnaphthalene is reduced by sodium and boiling amyl alcohol to 2 : 6-dimethyl-1,2,3-dihydronaphthalene, b. p. 125—126°/15 mm.; the constitution of the compound is deduced from the observation that it yields a liquid dibromide which is smoothly decomposed when distilled into hydrogen bromide and 2 : 6-dimethylnaphthalene. 1-Nitro-2 : 6-dimethylnaphthalene, yellow leaflets, m. p. 68°, is prepared by the action of nitric acid (*d* 1.51) on a solution of the hydrocarbon in glacial acetic acid at 70°. 1-Amino-2 : 6-dimethyl-

naphthalene crystallises in colourless needles, m. p. 91°; the corresponding *acetyl* derivative crystallises in lustrous needles, m. p. 211°, whereas the *benzoyl* derivative forms brown leaflets, m. p. 219—220°. Nitration of the mononitro-compound dissolved in concentrated sulphuric acid gives a *dinitro*-derivative, colourless needles, m. p. 186°, whereas in glacial acetic acid an isomeric *dinitro*-compound, slender, yellow needles, m. p. 179°, is obtained (the 1:4- or 1:5-position of the nitro-groups has not been elucidated for either compound). The latter compound is reduced by stannous chloride and hydrochloric acid to the corresponding *diamine*, dark red crystals, m. p. 158—159° (the *diacetyl* derivative is described). *Trinitro-2:6-dimethylnaphthalene*, slender, pale yellow needles, m. p. 243°, is isolated from the mother-liquors obtained by nitrating the mononitro-compound in glacial acetic acid solution.

The presence of a nitro-group in the ortho-position to the methyl radicle enables 1-nitro-2:6-dimethylnaphthalene to condense with ethyl oxalate in the presence of alcoholic sodium ethoxide to form 1-nitro-6-methylnaphthyl-2-pyruvic acid, $\text{NO}_2\cdot\text{C}_{10}\text{H}_7\text{Me}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$, pale brown needles, m. p. 195° (*methyl* ester, coarse brown needles, m. p. 119°; *oxime*, yellow needles, m. p. 176°). The substituted pyruvic acid is oxidised by hydrogen peroxide in the presence of sodium hydroxide to 1-nitro-6-methylnaphthyl-2-acetic acid, yellow crystals, m. p. 201° (*methyl* ester, m. p. 89°) and by potassium permanganate in alkaline solution to 1-nitro-6-methylnaphthalene-2-carboxylic acid, lustrous needles, m. p. 238—239°. The latter acid is reduced by ferrous sulphate to 1-amino-6-methylnaphthalene-2-carboxylic acid, pale yellow needles, m. p. 205—207°. Nitrous acid converts 1-nitro-6-methylnaphthylpyruvic acid into 1-nitro-6-methylnaphthyl-2-acetonitrile, pale yellow needles, m. p. 162°; apparently the nitrous acid is reduced to hydroxylamine, which then gives the oxime of the pyruvic acid derivative, the latter being decomposed into the nitrile, carbon dioxide, and water.

7-Methyl- α -naphthindole-2-carboxylic acid, $\text{C}_{10}\text{H}_7\text{Me}\cdot\text{C}\begin{smallmatrix} \text{NH} \\ \text{CH} \end{smallmatrix} > \text{CO}\cdot\text{CO}_2\text{H}$, colourless needles, m. p. 211°, is prepared by the reduction of 1-nitro-6-methylnaphthylpyruvic acid by ferrous sulphate and ammonia, and is purified conveniently through the *barium* salt; when heated at 220°, it yields 7-methyl- α -naphthindole, brown crystals, m. p. 143°. Decomposition of 1-nitro-6-methylnaphthylpyruvic acid by sodium hydroxide leads to the production of 1-nitro-6-methylnaphthyl-2-acetaldehyde, a yellow compound, m. p. about 212—213°, which is isolated in small amount by decomposing its bisulphite compound with cold dilute sulphuric acid; the corresponding *phenylhydrazone* crystallises in pale yellow leaflets, m. p. 156°. If decomposition of the bisulphite compound is effected with hot dilute sulphuric acid, 7-methyl- α -naphthisatin, slender red needles, m. p. 265° (*phenylhydrazone*, red needles, m. p. 275°) is immediately obtained. The reduction of 1-nitro-6-methylnaphthyl-2-acetic acid with ferrous sulphate gives 7-methyl- α -naphthoxindole, dark brown crystals, m. p. above 280°.

H. W.

Higher Terpene Compounds. VI. The two Methylisopropynaphthalenes from Cadalene. L. RUZICKA and M. MINGAZZINI (*Helv. Chim. Acta*, 1922, 5, 710—715).—The naphthoic acid, $C_{15}H_{16}O_2$, obtained by the oxidation of cadalene with chromic acid (this vol., i, 561) is now shown to be 6-methyl-4-isopropyl-1-naphthoic acid, since the methylisopropynaphthalene obtained on heating it with lime is different from the synthetic 1-methyl-4-isopropynaphthalene, which would have been formed had the acid had the only other possible structure, namely, 1-methyl-4-isopropyl-6-naphthoic acid. For the synthesis of 1-methyl-4-isopropynaphthalene, 1-methyl-2- β -bromoethyl-4-isopropylbenzene was condensed with ethyl malonate, giving ethyl β -2-cymylethylmalonate, $C_6H_3MePr^2 \cdot CH_2 \cdot CH_2 \cdot CH(CO_2Et)_2$, a viscous, colourless oil, b. p. 200—210°/12 mm. This was converted into γ -2-cymylbutyric acid, $C_6H_3MePr^2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, b. p. 195—200°/12 mm., and from this, by the action of thionyl chloride, the chloride, b. p. 165°/12 mm., was prepared, which, with aluminium chloride, gave 5-keto-1-methyl-4-isopropyltetrahydronaphthalene, b. p. 160—170°/12 mm.; semicarbazone, m. p. 178—180°. The keto-compound was reduced with zinc and hydrochloric acid to 1-methyl-4-isopropyl-5:6:7:8-tetrahydronaphthalene, b. p. 135—140°/12 mm. This was heated with sulphur to dehydrogenate it to 1-methyl-4-isopropynaphthalene, a nearly colourless oil, b. p. 135—145°/12 mm., picrate, orange-yellow needles, m. p. 99—100°. The hydrocarbon from the above naphthoic acid, that is, 6-methyl-4-isopropynaphthalene, gave a picrate, m. p. 101—102°, and a styphnate, m. p. 163—164°. It is shown that eudalin is not identical with the synthetic 1-methyl-4-isopropynaphthalene or with the 6-methyl-4-isopropyl compound from the naphthoic acid. Eudalin is probably not an apocadalene, as has been supposed. E. H. R.

Nitration of Hydrocarbons in Basic or Neutral Medium. M. BATTEGAY and Ph. BRANDT (*Bull. Soc. chim.*, 1922, [iv], 31, 910—915; cf. Wagner, A., 1886, 708; Verley, A., 1901, i, 143; Meisenheimer and Connerade, A., 1904, i, 391).—Anthracene and naphthalene may be nitrated by means of anhydrous pyridinium nitrate in presence of excess of pyridine. The products obtained are 9-nitroanthracene and α -nitronaphthalene; in the former case the yield represents 70% of the hydrocarbon used, in the latter, 40%. Other products of the reactions are anthraquinone and nitroanthrone from anthracene and 1-nitro-2:3-phthalic acid from naphthalene. The formation of nitroanthracene is explained by the authors on the hypothesis that nitrodihydroanthranol is first formed as an additive product and is then transformed into nitroanthracene with loss of water. H. J. E.

Action of Light on 9-Nitroanthracene. M. BATTEGAY, Ph. BRANDT and J. MORITZ (*Bull. Soc. chim.*, 1922, [iv], 31, 915—917; cf. preceding abstract).—9-Nitroanthracene is yellow in dilute alcoholic solution. On exposure to sunlight, the liquid becomes strongly fluorescent and smells of acetaldehyde. When the solution is sufficiently concentrated, nitrous acid is evolved and crystals of

anthraquinone are deposited. On shaking the solution in contact with air, the fluorescence disappears; when again exposed to sunlight it reappears, but more rapidly than at first. The fluorescence is due to photochemical reduction of anthraquinone, and is exhibited by alcoholic solutions of that substance; the reduction product is readily oxidised in air.

H. J. E.

Studies in the Anthracene Series. III. EDWARD DE BARRY BARNETT, JAMES WILFRED COOK, and HERBERT HENRY GRAINGER (T., 1922, **121**, 2059—2069).

The Solubility of Phenanthrene in Various Organic Solvents. HERBERT HENSTOCK (T., 1922, **121**, 2124—2128).

Action of Polyhalogenated Compounds of Methane and Ethane on Magnesyl [Magnesium Alkyl] Compounds. II.

R. BINAGHI (*Gazzetta*, 1922, **52**, ii, 132—138; cf. this vol., i, 313).—Both chloroform and bromoform react readily with magnesium phenyl bromide giving triphenylmethane, alone in the former case, and mixed with tetraphenylethane in the latter. The first phase of the reaction probably consists in the formation of the compound CHPh_2X , which then yields either triphenylmethane or tetraphenylethane or, with bromoform, the two together: $\text{CHPh}_2\text{Br} + \text{MgPhBr} = \text{MgBr}_2 + \text{CHPh}_3$, and $2\text{CHPh}_2\text{Br} + \text{MgPhBr} = \text{MgBr}_2 + \text{C}_6\text{H}_5\text{Br} + \text{CHPh}_2\text{CHPh}_2$. With all three trihalogenated derivatives of methane, bromobenzene also is formed, so that, even with chloroform, the formation of triphenylmethane is not represented by the equation $3\text{MgPhBr} + \text{CHCl}_3 = 3\text{MgClBr} + \text{CHPh}_3$.

The action of bromoform on magnesium ethyl bromide is analogous to that of iodoform, the products being acetylene, ethane, methane ethyl bromide, dibromomethane, and a small proportion of triethylmethane; a distinct odour resembling that of moulds is observed, especially after the final treatment of the products with water. The various reactions involved are probably $3\text{MgEtBr} + 2\text{CHBr}_3 = 3\text{MgBr}_2 + 3\text{C}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_2$; $\text{C}_2\text{H}_2 + 2\text{MgEtBr} = 2\text{C}_2\text{H}_6 + \text{MgBr}_2\text{C}\equiv\text{C}\cdot\text{MgBr}$; the latter $+ 2\text{H}_2\text{O} = 2\text{MgBr}\cdot\text{OH} + \text{C}_2\text{H}_2$; $\text{CHBr}_3 + \text{MgEtBr} = \text{C}_2\text{H}_5\text{Br} + \text{CHBr}_2\cdot\text{MgBr}$; the latter $+ \text{H}_2\text{O} = \text{MgBr}\cdot\text{OH} + \text{CH}_2\text{Br}_2$; $\text{CHBr}(\text{MgBr})_2 + 2\text{H}_2\text{O} = 2\text{MgBr}\cdot\text{OH} + \text{CH}_3\text{Br}$, and $\text{CH}(\text{MgBr})_3 + 3\text{H}_2\text{O} = 3\text{MgBr}\cdot\text{OH} + \text{CH}_4$.

Quite different is the interaction of chloroform and magnesium ethyl bromide, which yields methane, ethylene, and a small proportion of ethylene dibromide, but no acetylene, and gives a further evolution of gas when the products are treated with water. The mechanism of the reaction may be explained by the equations $\text{CHCl}_3 + 3\text{MgEtBr} = \text{CH}(\cdot\text{Cl}\cdot\text{MgEtBr})_3$, and $\text{CHCl}_3 + 3\text{MgEtBr} = 3\text{MgClBr} + 3\text{C}_2\text{H}_4 + \text{CH}_4$.

T. H. P.

Free Pentaphenylethyl. The Nature of the Carbon Linking. W. SCHLENK and HERMANN MARK (*Ber.*, 1922, **55**, [B], 2285—2299).—The preparation of free pentaphenylethyl is described. The usual method of preparing this type of free radicle could not be adopted primarily in this instance, owing to the impossibility

of converting pentaphenylethanol into pentaphenylethyl chloride and subsequently bringing the latter into reaction by a suitable method; the process adopted consists, therefore, essentially in the preparation of octaphenylpropane and decaphenylbutane, and taking advantage of the dissociability of these compounds into pentaphenylethyl and triphenylmethyl and pentaphenylethyl, respectively. The success of the operations is greatly facilitated by the unexpected completeness of the dissociation of the fully phenylated hydrocarbons into the radicles. *Pentaphenylethyl*, Ph_5CPh_2 , forms golden-yellow crystals with a metallic glance, and is particularly noteworthy, since it exists in solution practically entirely in the unimolecular condition. It may be regarded as triphenylmethyl in which one phenyl group is replaced by a triphenylmethyl residue. Since the free fourth carbon valency of triphenylmethyl is markedly weaker than the ordinary carbon valency, it follows that, if the principle of the equality of action and reaction be accepted, it can only make a relatively small affinity demand on the central carbon atom of the diphenylmethyl group, and that, in consequence, a relatively larger measure of affinity must remain for the two phenyl groups and the free valency. It would therefore be expected that the free valency of pentaphenylethyl would be relatively stronger than that of triphenylmethyl. The balance of the experimental evidence is directly against this view, so that the authors draw the conclusion that an equal demand is not necessarily made on the two carbon atoms of a C-C linking with respect to energy of combination.

An ethereal solution of sodium triphenylmethyl is treated with a similar solution of dichlorodiphenylmethane [benzophenone chloride] in an atmosphere of nitrogen. The solution is filtered from sodium chloride, somewhat concentrated, and cooled, whereupon a mixture of coarsely crystalline pentaphenylethyl and hexaphenylethane separates. The supernatant liquid containing suspended hexaphenylethane is decanted and the residual pentaphenylethyl is purified by repeated washing with cold absolute ether. In a somewhat similar manner, pentaphenylethyl is obtained by the action of triphenylmethyl chloride on disodium tetraphenylethane in the presence of anhydrous ether; the yield in this instance is poor, since the main reaction occurs in accordance with the scheme: $\text{CPh}_2\text{Na} \cdot \text{CPh}_2\text{Na} + 2\text{Ph}_3\text{CCl} \rightarrow 2\text{NaCl} + \text{Ph}_3\text{CPh}_2 + 2\text{CPh}_3$. Pentaphenylethyl combines readily with chlorine to form *chloropentaphenylethane*, which is hydrolysed with unusual ease and readily decomposed by rise in temperature into pentaphenylethyl and chlorine; it gives pentaphenylethyl when its ethereal solution is treated with copper-bronze. The successive action of sodium amalgam and water on pentaphenylethyl leads to the production of pentaphenylethane, m. p. 173° , $\text{CPh}_3\text{CPh}_2 \xrightarrow{+\text{Na}} \text{Ph}_3\text{CPh}_2\text{Na} \xrightarrow{\text{H}\cdot\text{OH}} \text{NaOH} + \text{CPh}_3\text{CHPh}_2$. H. W.

Analogues of Pentaphenylethyl. W. SCHLENK and HERMANN MARK (*Ber.*, 1922, **55**, [B], 2299—2302).—In the triphenylmethyl series, it has been shown that the position of the dissocia-

tion equilibrium is largely dependent on the nature of the aryl groups, and that the tendency towards dissociation is greatly increased by the substitution of the biphenyl for the phenyl group. In the pentaphenylethyl series, this does not appear to be the case, since triphenylbiphenylethyl, like the parent radicle (preceding abstract), exists entirely in the unimolecular condition in solution. Possibly with the pentaphenyl derivative the tendency towards dissociation is so powerful that it is unaffected by comparatively slight alterations in structure.

Triphenylbiphenylethyl, comparatively large, violet prisms, is prepared by the gradual addition of an ethereal solution of fluorone chloride to a solution of sodium triphenylmethyl in an atmosphere of nitrogen; in consequence of its relatively sparing solubility in ether, the separation of the new radicle from simultaneously formed triphenylmethyl is readily effected. It is converted by treatment with chlorine dissolved in chloroform into *triphenylbiphenylene-ethyl chloride*, from which the radicle is regenerated by agitation with copper powder. The chloride is hydrolysed with great readiness. It is dissociated in sunlight at the atmospheric temperature into its components which reunite when preserved in the absence of light.

H. W.

Aromatic Chloroamines. II. STEFAN GOLDSCHMIDT and LUDWIG STROHMENGER (*Ber.*, 1922, **55**, [B], 2450–2470).—The preparation of the very unstable di-*o*-chloroaniline has been described previously (Goldschmidt, A., 1913, i, 1173). The observations have now been extended to a number of its derivatives. The presence of negative substituents increases the stability of the molecule, which reaches its maximum in the case of di-*o*-chloropentachloroaniline which may be preserved unchanged for weeks at the atmospheric temperature if moisture is completely excluded. Positive substituents, on the other hand, diminish the stability of the molecule. The chemical behaviour of the compounds is completely in accord with the hypothesis that a radicle, $R\dot{N}$, is primarily formed. In every instance, polymerides of this radicle are ultimately isolated, either solely as azo-compounds or as mixtures of these with *N*-arylquinonedi-imides, according to the choice of the amine. The same products are obtained by the action of oxidising agents on aniline and its homologues (cf. Goldschmidt, A., 1920, i, 226) when such oxidation is possible, thus giving renewed support to the hypothesis that both types of reaction take place through the same intermediate product, the radicle $R\dot{N}$.

An improved process for obtaining an ethereal solution of hypochlorous acid (cf. Wohl, A., 1907, i, 194) is described.

Di-*o*-chloro-*p*-nitroaniline, $\text{NO}_2\cdot\text{C}_6\text{H}_3\cdot\text{NCl}_2$, is prepared by the action of hypochlorous acid on *p*-nitroaniline in ethereal solution at 20° (the necessary manipulation and apparatus are described in detail). It forms reddish-yellow prisms which can be preserved unchanged during several days at -80°, but decompose rapidly at the atmospheric temperature, ultimately exploding and leaving

a residue containing 4:4'-dinitroazobenzene. Its melting point, determined in a pre-heated bath, is about 50°. It is decomposed by ethereal hydrogen chloride solution into 2:6-dichloro-*p*-nitroaniline, m. p. 189—190°, and by aqueous alcoholic potassium iodide solution into 4:4'-dinitroazobenzene, m. p. 222° after softening at 219°, which is also obtained by the action of a solution of ammonia in ether and of an alcoholic solution of sodium ethoxide. The auto-decomposition of di-*o*-chloro-*p*-nitroaniline, dissolved in ether, light petroleum, acetic anhydride, or ethyl benzoate, gives varying proportions of 4:4'-dinitroazobenzene and 2:6-dichloro-*p*-nitroaniline.

Di-o-chloro-o-nitroaniline, pale yellow to brown prisms, m. p. (in pre-heated bath) 48—50° (complete decomp.) is prepared in the same manner as the para-isomeride. It can be preserved unchanged at a low temperature, but decomposes with ultimate explosion at the atmospheric temperature. In ethereal solution, it decomposes slowly at the ordinary temperature with production of 4:6-dichloro-*o*-nitroaniline, whereas in boiling carbon tetrachloride it yields chlorine, hydrogen chloride, and 2:2'-dinitroazobenzene, m. p. 209—210° after softening at 207°. It is converted by ethereal hydrogen chloride in the absence of an excess of hypochlorous acid into 4-chloro-*o*-nitroaniline, m. p. 115°, and a brown liquid which has not been further examined, whereas if hypochlorous acid is present in excess it gives 4:6-dichloro-*o*-nitroaniline, m. p. 101—102°; sodium thiosulphate solution transforms it into 2:2'-dinitroazobenzene.

Di-o-chloro-m-nitroaniline is prepared in the same manner as the ortho- and para-isomerides, to which it exhibits close similarity; it is converted by alcoholic sodium ethoxide solution or copper powder into 3:3'-dinitroazobenzene, m. p. 149—150°.

Di-o-chloro- α - ψ -cumidine [1-dichloroamino-2:3:5-trimethylbenzene] is prepared from hypochlorous acid and α - ψ -cumidine in ethereal solution, but is too unstable to permit isolation as a solid. It is converted by the successive action of a large excess of potassium iodide solution and zinc dust and glacial acetic acid into *chloroaminodicyumylamine*, colourless needles, m. p. 167—168° (which is partly transformed by distillation with steam into 4(?)-chloro-2:3:5-trimethylaniline), colourless needles, m. p. 110.5—111° and 4:4'(?)-dichloro-2:3:5:2':3':5'-hexamethylazobenzene, lustrous, red needles, m. p. 189—190°. Chloroaminodicyumylamine, dissolved in light petroleum, is transformed by lead peroxide into *chlorocumylcumoquinonedi-imide*, $C_6HMe_3Cl \cdot N : C_6HMe_3 \cdot NH$, dark red, oblique prisms, m. p. 113—116°, the constitution of which is elucidated from its conversion into 4(?)-chloro-2:3:5-trimethylbenzene and cumoquinol.

Di-o-chloro-m-toluidine resembles the compound just described in that it can only be isolated in solution. It is converted by aqueous alcoholic potassium iodide solution and subsequent treatment with zinc dust into *aminoditolylamine*, prisms, m. p. 121°; 6-chloro-3-aminotoluene, colourless crystals, m. p. 83.5—84°; and 4:4'(?)-dichloro-3:3'-dimethylazobenzene, lustrous, yellow needles,

m. p. 162–163°. *m-Tolyltoluquinonedi-imide* could not be isolated in the crystalline condition by the action of lead peroxide in the presence of sodium sulphate on an ethereal solution of aminoditolylamine.

Detailed directions are given for the conversion of 2 : 6-dichloro-*p*-nitroaniline into 5-nitro-*m*-dichlorobenzene, for the reduction of the latter to 3 : 5-dichloroaniline and the chlorination of the base to 2 : 3 : 4 : 5 : 6-pentachloroaniline, m. p. 232°. The pentachloro-compound is transformed by hypochlorous acid in ethereal solution into *di- ω -chloropentachloroaniline*, pale yellow, transparent, thin prisms, m. p. 111° (decomp.). This substance behaves towards neutral or acid potassium iodide solution in the same manner as the chloroamines described previously. In boiling toluene solution, it is decomposed into *decachloroazobenzene*, dark red, lustrous plates or flesh-coloured needles, m. p. 317–318° after softening at 316°.

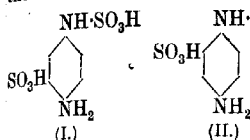
H. W.

The Action of Sodium Hydrogen Sulphite on the Nitroanilines. HUGO WEIL and PAUL WASSERMANN (*Ber.*, 1922, 55, [B], 2533–2542; cf. Weil and Moser, this vol., i, 443).—An extension of previous work to the nitroanilines and related compounds.

p-Nitroacetanilide is converted by a boiling aqueous solution of sodium hydrogen sulphite (40%) into *sodium p-acetylamino-phenylsulphamate*, $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{SO}_3\text{Na}\cdot\text{H}_2\text{O}$; the corresponding *benzidine* salt, $\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_4(\text{SO}_3)_2\text{H}_2\text{O}$, α -*naphthylamine* salt ($+\text{H}_2\text{O}$), and β -*naphthylamine* salt ($+\text{H}_2\text{O}$) are described. *p*-Acetylaminophenylsulphamic acid is converted by boiling aqueous sodium hydroxide into *p-aminophenylsulphamic acid*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{SO}_3\text{H}$, colourless crystals, whereas boiling dilute mineral acids transform it into acetyl-*p*-phenylenediamine. Sodium *p-aminophenylsulphamate* condenses with chloro-2 : 4-dinitrobenzene to give the salt, $\text{C}_{12}\text{H}_8\text{O}_4\text{N}_4\text{SO}_3\text{Na}$, a red, crystalline substance; the corresponding *barium* salt is sparingly soluble in water. *p*-Aminophenylsulphamic acid can be diazotised, and the diazonium compound couples with β -naphthol to give an *azo-dye* which retains the *N*-sulphonic group. *p*-Nitro-*o*-acetotoluidide and *p*-nitro-*o*-acetaniside are reduced by sodium hydrogen sulphite, but the products are respectively too soluble and too unstable to permit their isolation in the homogeneous condition.

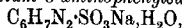
p-Nitrobenzanilide, which is most conveniently prepared from *p*-nitroaniline and benzoyl chloride in the presence of pyridine, is reduced similarly to, but much more slowly than, the corresponding acetyl derivative, forming *sodium p-benzoylamino-phenylsulphamate*, $\text{C}_{13}\text{H}_{11}\text{ON}_2\text{SO}_3\text{Na}\cdot 2\text{H}_2\text{O}$, which is relatively sparingly soluble in water. *Sodium p-benzoylamino-*o*-tolylsulphamate* is prepared in a similar manner. Benzylated nitroanilines cannot be reduced with sodium hydrogen sulphite. *p*-Nitroaniline is gradually dissolved by a boiling solution of sodium hydrogen sulphite, but a sulphamic acid cannot be isolated, although its presence can be detected. If, however, the solution is greatly concentrated and acidified with dilute hydrochloric acid, it yields

the monosodium salt of a sulphamsulphonic acid (annexed formula



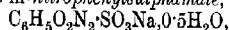
I or II) (the corresponding β -naphthylamine salt is described) which loses a sulphonic group under the influence of hydrochloric acid and forms *p*-phenylenediaminesulphonic acid. Although it contains a

primary amino-group, it does not react with benzoyl chloride or chloro-2:4-dinitrobenzene, possibly because of the presence of the sulphonic group in the ortho-position to the amino-group (formula I). In harmony with these observations, the free amino-group is not affected by nitrous acid; the compound can be diazotised and the diazonium compound couples with β -naphthol to form a dye, but the amino-group which takes part in the change is that which is formed by the loss of a sulphonic group from the compound. *p*-Nitro-*o*-toluidine is converted similarly into sodium amino-*o*-tolyl-*p*-sulphamsulphonate, $\text{SO}_3\text{H}\cdot\text{C}_7\text{H}_6\text{N}_2\cdot\text{SO}_3\text{Na}\cdot 0.5\text{H}_2\text{O}$. *o*-Nitroaniline, on the other hand, is transformed into sodium *o*-aminophenylsulphamate,



colourless, lustrous crystals. The products of the reduction of *m*-nitroaniline with sodium hydrogen sulphite are too soluble to permit their isolation, but they can be diazotised in solution and subsequently coupled with β -naphthol; the azo-dye thus formed is acidic in character and retains this property after being boiled with mineral acid, although it loses sulphuric acid under these conditions. It appears, therefore, that a sulphosulphamic acid is formed initially.

m-Dinitrobenzene is reduced by sodium hydrogen sulphite to a mixture of sodium *m*-nitrophenylsulphamate,



and sodium *m*-phenylenedisulphamate, $\text{C}_6\text{H}_6\text{N}_2(\text{SO}_3\text{Na})_2\cdot 3.5\text{H}_2\text{O}$.

H. W.

Nitro-derivatives of *m*-Nitrodimethylaniline. AQUILA FORSTER and WILLIAM COULSON (T., 1922, 121, 1988—1997).

Bases obtained in the Decomposition of the Azides of Thiocarbamic Acids. E. OLIVERI-MANALÀ (*Gazzetta*, 1922, 52, ii, 98—103; cf. A., 1921, i, 900).—By heating azides of thiocarbamic acids with concentrated hydrochloric acid, the author as previously (A., 1914, i, 1144) obtained in the free state some of the bases described by Freund and Schwarz (A., 1897, i, 125) as thiocyanamides, $\text{NHR}\cdot\text{CS}\cdot\text{N}_3 \rightarrow \text{NHR}\cdot\text{CSN}$. As regards both their genesis and their constitution, these bases exhibit close analogy to Wieland's nitrile oxides (A., 1907, i, 527; 1909, i, 216, 17, 923). This analogy extends also to the anomalous cryoscopic behaviour, compounds of both classes exhibiting in solution molecular weights considerably higher than the calculated values, owing probably to polymerisation. The bases in question differ, however, from the nitrile oxides, which may also undergo isomeric

change to the corresponding esters of isocyanic acid, in that, when heated with water or a dilute mineral acid or an organic solvent, they readily lose the sulphur atom, giving polymerides of the corresponding derivatives of cyanamide, $3\text{NHR}\cdot\text{C}\cdot\text{N}\cdot\text{S} \rightarrow (\text{NHR}\cdot\text{CN})_3$; on the other hand, the nitrile oxides lose the oxygen atom by reduction, yielding nitriles, $\text{R}\cdot\text{CNO} + \text{H}_2 = \text{H}_2\text{O} + \text{R}\cdot\text{CN}$.

The constitution of these bases is most probably represented by the formula $\text{NHR}\cdot\text{C}\cdot\text{N}\cdot\text{S}$, and it is proposed to name the compound $\text{NHPh}\cdot\text{C}\cdot\text{N}\cdot\text{S}$, anilinesulphonitrile, rather than phenylthiocyanamide.

o-Toluidinesulphonitrile, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{C}\cdot\text{N}\cdot\text{S}$, obtained by prolonged boiling of the corresponding azide (A., 1921, i, 900) with concentrated hydrochloric acid, forms crystals, m. p. 138–140°, and shows abnormally high molecular weight in freezing acetic acid. The *hydrochloride* and *platinichloride* were analysed.

p-Toluidinesulphonitrile, similarly prepared, was obtained crystalline, and the *hydrochloride* and *platinichloride* were prepared.

Anilinesulphonitrile, $\text{C}_7\text{H}_7\text{N}_2$ (cf. A., 1914, i, 1144) has m. p. 122–123° and exhibits high molecular weight in acetic acid. The *hydrobromide* and *platinichloride* were prepared.

Ethylaminesulphonitrile, $\text{NHEt}\cdot\text{C}\cdot\text{N}\cdot\text{S}$, was not prepared in the free state owing to the readiness with which it decomposes, but is obtained as *hydrochloride* when the azide of carbamic acid is boiled with concentrated hydrochloric acid; the *platinichloride* was also prepared. The azide of thiocarbamic acid, $\text{NHEt}\cdot\text{CS}\cdot\text{N}_3$, obtained by the interaction of ethylthiocarbimide and azoimide in ethereal solution, is identical with the compound prepared by Freund and Schwarz (*loc. cit.*) by the action of nitrous acid on ethylthiosemicarbazide and termed triazosulphole, $\text{NHEt}\cdot\text{C} \begin{smallmatrix} \text{N}\cdot\text{N} \\ | \quad | \\ \text{S}\cdot\text{N} \end{smallmatrix}$.

with mercuric oxide, it yields, not the corresponding azide of carbamic acid, but the additive compound, $\text{C}_3\text{H}_6\text{N}_4\text{S}_2\text{HgO}$, which crystallises in needles.

T. H. P.

The Condensation of Aromatic *o*-Aminosulphonic Acids with isoCyanic Acid. JOHN RICHARD SCOTT and JULIUS BEREND COHEN (T., 1922, 121, 2034–2051).

Electrolytic Reactions of Naphthalene and its Derivatives.
III. Electrolytic Oxidation of α -Naphthylamine and α -Tetrahydro- α -naphthylamine. KASHICHI OXO (*Mem. Coll. Sci. Kyoto*, 1922, 5, 345–357; cf. A., 1921, i, 334, 726).—The electrolytic oxidation of α -naphthylamine has been examined in a divided cell in which a small sheet lead cathode is immersed in sulphuric acid (20%) and the anode liquid is a solution of α -naphthylamine in acetone and dilute sulphuric acid. Platinum, graphite, and lead peroxide, respectively, are used as anode materials, the last-named giving the best results. Under these conditions, α -naphthylamine is converted into a mixture of naphthylamine-violet and α -naphthoquinone. Its behaviour thus differs from that of aniline, which, at a platinum electrode, is transformed solely into aniline-black.

but the apparent stability of the latter may be due entirely to its solubility in the anode liquid. The current yield diminishes with increasing current density and attains its maximum at approximately 1 ampere per 100 sq. cm. Elevation of the electrolytic temperature does not necessarily favour the yield. A suitable concentration of sulphuric acid is 10–30%, the best results being observed with a 10% solution. Potassium chromate, chrome alum, potassium chlorate, and ferric sulphate act effectively as oxygen carriers. The possibility of the formation of 4-amino- α -naphthol as an intermediate product of the oxidation of α -naphthylamine is discussed, but its production could not be established experimentally.

The electrolytic oxidation of *ar*-tetrahydro- α -naphthylamine has been examined under closely similar conditions; it is converted mainly into *ar*-tetrahydro- α -naphthaquinone. Platinum, lead peroxide, and graphite are used as anode material, and of these lead peroxide gives the best results. The most suitable conditions are a current density of about 1 amp./100 sq. cm., a temperature between 18° and 23°, and a concentration of sulphuric acid between 10% and 30%. Chrome alum, potassium chromate, potassium chlorate, and potassium ferrocyanide are efficient oxygen carriers.

H. W.

Preparation of Symmetrical Tetra-substituted Carbamides.

ARTHUR PERCIVAL TANBERG and HERBERT WINKEL (E. J. DU PONT DE NEMOURS & Co.) (Brit. Pat. 144681; from *Chem. Zentr.*, 1922, ii, 1136).—Secondary aromatic amines, dissolved in indifferent solvents such as benzene, xylene, solvent naphtha, or carbon tetrachloride, are heated at 70° and treated with the necessary amount of carbonyl chloride. *s*-Diphenyldimethylcarbamide is thus prepared from methylaniline according to the equation $4\text{NHMePh} + \text{COCl}_2 = \text{CO}(\text{NMePh})_2 + 2\text{NH}_2\text{MePhCl}$. G. W. R.

The Chlorohydrin and Oxide of Methylenecyclobutane and the Transformation of the Former into cyclopentanone.

N. J. DEMJANOV and MARIE DOJARENKO (*Ber.*, 1922, 55, [B], 2730–2737).—Methylenecyclobutane (cf. this vol., i, 996) is converted by hypochlorous acid into the corresponding *chlorohydrin*, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{C}(\text{OH})\cdot\text{CH}_2\text{Cl}$ or $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{CCl}\cdot\text{CH}_2\cdot\text{OH}$, b. p. 64.5°/20 mm., 75°/33 mm., 83°/47 mm., 158°/747 mm., d_4^{25} 1.1657, d_4^{25} 1.1502, d_4^{25} 1.1448, n_D^{25} 1.4657. The corresponding *phenylurethane* crystallises in needles, m. p. 112.5–113°. When heated under a reflux condenser with water and lead oxide, the chlorohydrin is converted into *cyclopentanone*, which is identified as the oxime and semicarbazone; the same reaction takes place very slowly at the atmospheric temperature. Glutaric and succinic acids are produced by the action of nitric acid (d 1.2) on the chlorohydrin. Concentrated aqueous potassium hydroxide solution converts the chlorohydrin into the *oxide*, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{C}\langle\begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}\rangle$, b. p.

(1 mol. : 2 mol.), m. p. 171.5° , which forms a eutectic with 2 : 6-dihydroxynaphthalene at 165° containing 41%, and one with β -naphthylamine at 109° containing 98%, of β -naphthylamine. 2 : 7-Dihydroxynaphthalene and β -naphthylamine give a *compound* (1 mol. : 1 mol.), m. p. 163° , which forms a eutectic with 2 : 7-dihydroxynaphthalene at 153° containing 36%, and one with β -naphthylamine at 108° containing 98.5%, of β -naphthylamine.

1 : 5-Dihydroxynaphthalene and α -naphthylamine give a eutectic at 44° containing 95% of α -naphthylamine. 2 : 6-Dihydroxynaphthalene and α -naphthylamine give a eutectic at 46° containing 98% of α -naphthylamine. 2 : 7-Dihydroxynaphthalene and α -naphthylamine give a eutectic at 35° containing 91% of α -naphthylamine. 1 : 4-Dihydroxynaphthalene and α -naphthylamine give a *compound* (1 mol. : 1 mol.), m. p. 143° , which forms a eutectic with 1 : 4-dihydroxynaphthalene at 129° containing 39%, and one with α -naphthylamine at 44° containing 94%, of α -naphthylamine. 1 : 6-Dihydroxynaphthalene and α -naphthylamine give a *compound* (2 mols. : 3 mols.), m. p. 84.5° , which forms a eutectic with 1 : 6-dihydroxynaphthylamine at 76° containing 53%, and one with α -naphthylamine at 43° containing 92.5%, of α -naphthylamine. 1 : 8-Dihydroxynaphthalene and α -naphthylamine give a *compound* (1 mol. : 1 mol.), m. p. 76.5° , which forms a eutectic with 1 : 8-dihydroxynaphthalene at 74° containing 45%, and one with α -naphthylamine at 41° containing 84%, of α -naphthylamine. 2 : 3-Dihydroxynaphthalene and α -naphthylamine give a *compound* (2 mols. : 3 mols.), m. p. 103° , which forms a eutectic with 2 : 3-dihydroxynaphthalene at 97° containing 54.5%, and one with α -naphthylamine at 35° containing 87%, of α -naphthylamine.

1 : 6-Dihydroxynaphthalene and *p*-phenylenediamine give a *compound* (1 mol. : 1 mol.), m. p. 170° , which forms a eutectic with 1 : 6-dihydroxynaphthalene at 121° containing 15%, and one with *p*-phenylenediamine at 125° containing 93%, of *p*-phenylenediamine. 1 : 8-Dihydroxynaphthalene and *p*-phenylenediamine form a *compound* (2 mols. : 1 mol.), m. p. 118° , which gives a eutectic with 1 : 8-dihydroxynaphthalene at 109° containing 21%, and one with *p*-phenylenediamine at 106° containing 37%, of *p*-phenylenediamine. 2 : 3-Dihydroxynaphthalene and *p*-phenylenediamine form a *compound* (2 mols. : 1 mol.), m. p. 164° , which gives a eutectic with 2 : 3-dihydroxynaphthalene at 141° containing 1%, and one with *p*-phenylenediamine at 118° containing 70%, of *p*-phenylenediamine. 2 : 6-Dihydroxynaphthalene and *p*-phenylenediamine give a *compound* (1 mol. : 1 mol.), m. p. 212° , which gives a eutectic with 2 : 6-dihydroxynaphthalene at 195° containing 10%, and one with *p*-phenylenediamine at 140° containing 95%, of *p*-phenylenediamine. 2 : 7-Dihydroxynaphthalene and *p*-phenylenediamine give a *compound* (2 mols. : 1 mol.), m. p. 180° , which forms a eutectic with 2 : 7-dihydroxynaphthalene at 171° containing 10.5%, and one with *p*-phenylenediamine at 129° containing 81%, of *p*-phenylenediamine.

1 : 4-Dihydroxynaphthalene and *m*-phenylenediamine give a *compound* (1 mol. : 1 mol.), m. p. 124° , which forms a eutectic with

m-phenylenediamine at 55° containing 92.5% of *m*-phenylenediamine. 1:6-Dihydroxynaphthalene and *m*-phenylenediamine give a compound (1 mol. : 1 mol.), m. p. 125°, which forms a eutectic with 1:6-dihydroxynaphthalene at 87° containing 22%, and one with *m*-phenylenediamine at 49° containing 89%, of *m*-phenylenediamine. 1:8-Dihydroxynaphthalene and *m*-phenylenediamine give a compound (1 mol. : 1 mol.), m. p. 101°, which forms a eutectic with 1:8-dihydroxynaphthalene at 75° containing 32%, and one with *m*-phenylenediamine at 58° containing 92%, of *m*-phenylenediamine. 2:3-Dihydroxynaphthalene and *m*-phenylenediamine give a compound (1 mol. : 1 mol.), m. p. 149°, which forms a eutectic with 2:3-dihydroxynaphthalene at 122° containing 24%, and one with *m*-phenylenediamine at 53° containing 94%, of *m*-phenylenediamine. 2:6-Dihydroxynaphthalene and *m*-phenylenediamine give a compound (1 mol. : 1 mol.), m. p. 171°, which forms a eutectic with 2:6-dihydroxynaphthalene at 125° containing 35%, and one with *m*-phenylenediamine at 61° containing 98%, of *m*-phenylenediamine. 2:7-Dihydroxynaphthalene and *m*-phenylenediamine give a compound (1 mol. : 1 mol.), m. p. 139°, which forms a eutectic with 2:7-dihydroxynaphthalene at 126° containing 33%, and one with *m*-phenylenediamine at 53° containing 98%, of *m*-phenylenediamine.

The system 1:4-dihydroxynaphthalene-*o*-phenylenediamine has a eutectic at 87° containing 83% of *o*-phenylenediamine. The system 2:3-dihydroxynaphthalene-*o*-phenylenediamine has a eutectic at 96° containing 93% of *o*-phenylenediamine. The formation of a compound in these cases was not proved. 1:6-Dihydroxynaphthalene and *o*-phenylenediamine give a compound (1 mol. : 1 mol.), m. p. 95°, which forms a eutectic with 1:6-dihydroxynaphthalene at 76° containing 32%, and one with *o*-phenylenediamine at 62° containing 61%, of *o*-phenylenediamine. 1:8-Dihydroxynaphthalene and *o*-phenylenediamine give a compound (1 mol. : 1 mol.), m. p. 151°, which forms a eutectic with 1:8-dihydroxynaphthalene at 117° containing 7%, and one with *o*-phenylenediamine at 93° containing 85%, of *o*-phenylenediamine. 2:6-Dihydroxynaphthalene and *o*-phenylenediamine give a compound (2 mols. : 3 mols.), m. p. 150°, which forms a eutectic with 2:6-dihydroxynaphthalene at 124° containing 30%, and one with *o*-phenylenediamine at 99° containing 92%, of *o*-phenylenediamine. 2:7-Dihydroxynaphthalene and *o*-phenylenediamine give a compound (2 mols. : 3 mols.), m. p. 140°, which forms a eutectic with 2:7-dihydroxynaphthalene at 101° containing 38%, and one with *o*-phenylenediamine at 96° containing 91%, of *o*-phenylenediamine.

1:4-Dihydroxynaphthalene and benzamide give a eutectic at 91° containing 61.5% of benzamide. 1:5-Dihydroxynaphthalene and benzamide form a eutectic at 106° containing 72% of benzamide. 1:1-Dihydroxynaphthalene and benzamide form a eutectic at 90° containing 45% of benzamide. 1:8-Dihydroxynaphthalene and benzamide form a eutectic at 46° containing 46% of benzamide. 2:6-Dihydroxynaphthalene and benzamide form a eutectic at 87° containing 48% of benzamide. 2:7-Dihydroxynaphthalene and

benzamide form a eutectic at 78° containing 52% of benzamide. 2:3-Dihydroxynaphthalene and benzamide give a compound (1 mol. : 3 mols.), m. p. 113°, which gives a eutectic with 2:3-dihydroxynaphthalene at 80° containing 48%, and one with benzamide at 106° containing 75%, of benzamide. C. K. I.

Synthesis of 1:12-Dihydroxyperylene and Perylene. ALOIS ZINCKE and RUPERT DENGK (*Monatsh.*, 1922, 43, 125—128).—Most of the work detailed in this paper has been described previously (this vol., i, 132). 1:12-Dibenzoyloxyperylene forms brownish-yellow, amorphous flocks, and decomposes at about 224°. C. K. I.

The Valency Problem of Sulphur. VII. o-Nitrophenyl-dithiochloride. HANS LECHER and KURT SIMON (*Ber.*, 1922, 55, [B], 2423—2432).—In a recent communication, the analogy between dithiochlorides, ArS_2Cl , and diazonium chlorides, ArN_2Cl , has been indicated (A., 1920, i, 860). Further examination of o-nitrophenyl dithiochloride shows that the similarity is purely formal and that the dithiochloride does not exhibit the typical properties of diazonium compounds. o-Nitrophenyldithiochloride is not a salt, since its solutions in ethylene chloride are non-conductors of electricity; it belongs to the relatively small class of sulphides in which bivalent sulphur functions as a positive element and in which its linkings are not heteropolar and ionisable. The preparation of o-nitrophenyl mercaptan, m. p. 57—58°, from *oo'*-dinitrodiphenyl disulphide and dextrose, is described in detail.

o-Nitrophenyl dithiochloride, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}_2\text{Cl}$, is stable at the atmospheric temperature; when heated by itself, it suffers incipient decomposition at about 100°, evolves sulphur chloride at about 150°, and explodes above 200°. It appears to be hydrolysed by water in accordance with the equation $2\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}_2\text{Cl} + \text{H}_2\text{O} \rightarrow (\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}_2)_2\text{O} + 2\text{HCl}$, but attempts to isolate the oxide in a homogeneous condition were not successful. Aqueous potassium hydroxide decomposes it according to the scheme $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}_2\text{Cl} + 2\text{KOH} \rightarrow \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SK} + (\text{HO}\cdot\text{S}\cdot\text{OH}) + \text{KCl}$. It reacts with dimethylaniline dissolved in anhydrous ether to form 4-dimethylaminophenyl 2'-nitrophenyl disulphide, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, orange-coloured plates, m. p. 115.5—117° (corr.).

2:2'-Dinitrodiphenyl trisulphide, yellow needles, m. p. 174.5—176° (corr.) when rapidly heated and placed in a pre-heated bath, is prepared by mixing ethereal solutions of o-nitrophenyl dithiochloride and o-nitrophenyl mercaptan. It could not be obtained satisfactorily from the mercaptan and sulphur dichloride or from o-nitrophenyl thiochloride and hydrogen sulphide. It is hydrolysed by concentrated aqueous potassium hydroxide at 70—80° in accordance with the equation $(\text{NO}_2\cdot\text{C}_6\text{H}_4)_2\text{S}_3 + 2\text{KOH} = 2\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SK} + (\text{HO}\cdot\text{S}\cdot\text{OH})$. o-Nitrophenyl dithiochloride reacts with piperidine, but the expected mixed disulphide, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}_2\cdot\text{C}_5\text{H}_{10}$, could not be isolated in a well-defined condition. H. W.

Vinylcyclopropane, certain Derivatives of Methylcyclopropylcarbinol and the Isomerisation of the cycloPropane Ring. N. J. DEMJANOV and MARIE DOJARENKO (*Ber.*, 1922, 55,

[B], 2718—2727).—Acetylcyclopropaneoxime, $\begin{matrix} \text{CH}_3 \\ \diagup \\ \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{CMe} \cdot \text{N} \cdot \text{OH}$,

is reduced to the corresponding amine, which is transformed by methyl iodide into trimethyl-2-cyclopropylethylammonium iodide. The hydroxide corresponding with the latter compound decomposes when distilled mainly into vinylcyclopropane, $\begin{matrix} \text{CH}_2 \\ \diagup \\ \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{CH} \cdot \text{CH}_2$,

a colourless, mobile liquid, b. p. 40—40.2°/755 mm., d_4^{20} 0.741, d_4^{25} 0.731, d_4^{30} 0.726, d_4^{35} 0.723, n_D^{20} 1.4205, n_D^{25} 1.4172. α -cycloPropyl-

ethyl-dimethylamine, $\begin{matrix} \text{CH}_2 \\ \diagup \\ \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{CHMe} \cdot \text{NMe}_2$, is produced in very

small amount during the action and is characterised in the form of its *picrate*, yellow needles, m. p. 187—188°, and *aurichloride*, thin, yellow, rectangular leaflets. Vinylcyclopropane reacts vigorously with bromine to give the corresponding *tribromide*, b. p. 86—88°/21—22 mm., d_4^{20} 1.842, d_4^{25} 1.825, d_4^{30} 1.818, n_D^{20} 1.54447, which reacts only very slowly with bromine. The hydrocarbon is oxidised by potassium permanganate at 0—5° to formic acid, cyclopropanecarboxylic acid and cyclopropylethylene glycol, $\begin{matrix} \text{CH}_2 \\ \diagup \\ \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$, b. p. 213—215°/750 mm., d_4^{20} 1.0823, d_4^{25} 1.0677, n_D^{20} 1.4637.

Methylcyclopropylcarbinol is transformed by iodine and red phosphorus into the *iodide*, $\text{C}_5\text{H}_9\text{I}$, a colourless liquid which becomes brown when preserved, b. p. 57.5—58.5°/19—20 mm., 69—70°/36 mm., d_4^{20} 1.597, d_4^{25} 1.575, d_4^{30} 1.5675, n_D^{20} 1.5244, n_D^{25} 1.5221; a specimen prepared by the action of hydrogen iodide on the carbinol at 0° had b. p. 68°/35 mm., d_4^{20} 1.6083, d_4^{25} 1.587, d_4^{30} 1.579, R 37.34. The iodide is converted by alcoholic potassium hydroxide solution into piperylene, $\text{CHMe} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2$, b. p. 41.8—42.2°/748 mm., d_4^{20} 0.697, d_4^{25} 0.688, d_4^{30} 0.6827, n_D^{20} 1.4366, n_D^{25} 1.43398, which is transformed by bromine into $\alpha\beta\gamma\delta$ -tetrabromo-*n*-pentane, long prisms, m. p. 116°. It appears, therefore, that the iodide, $\text{C}_5\text{H}_9\text{I}$, must have the constitution $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CHI} \cdot \text{CH}_3$ or $\text{CH}_3 \cdot \text{CH} \cdot \text{CH} \cdot \text{CHI} \cdot \text{CH}_3$ (probably the former), and that the cyclopropyl ring must have suffered fission during the action.

The action of dehydrating agents (acetic anhydride, oxalic acid, and phosphoric oxide) on the carbinol has been examined in the hope of obtaining vinylcyclopropane in this manner. A definite result is obtained only with acetic anhydride which gives the corresponding *acetate*, b. p. 138—139°/747 mm., d_4^{20} 0.949, d_4^{25} 0.939, d_4^{30} 0.931, n_D^{20} 1.4200, n_D^{25} 1.4182. H. W.

Ketens. XL. Ketenacetals. H. STAUDINGER and G. RATHSAM (*Helv. Chim. Acta*, 1922, 5, 645—655).—The preparation and examination of phenylketenacetal have shown that this is much more stable than the corresponding keten. Attempts were first

made to obtain the acetals of ordinary keten and of methylketen by heating the ortho-esters of acetic and propionic acids with phosphoric oxide, according to the scheme $\text{CH}_3\cdot\text{C}(\text{OEt})_2 \rightarrow \text{CH}_2\cdot\text{C}(\text{OEt})_2 + \text{EtOH}$, but without success. On the other hand, the ortho-ester of phenylacetic acid gave a good yield of phenylketenacetal when it was distilled several times at 12–15 mm. pressure. *Phenylketenacetal*, $\text{CHPh}\cdot\text{C}(\text{OEt})_2$, boils at $136^\circ/12$ mm. Compared with phenylketen, it is quite stable, and only polymerises very slowly at 130° . It is not oxidised by air at the ordinary temperature, but is very sensitive to water, giving ethyl phenylacetate; with bromine it gives ethyl phenylbromoacetate. It combines with 2 mols. of diphenylketen to form a compound, probably a cyclohexane derivative, $\text{C}_{40}\text{H}_{36}\text{O}_4$, white crystals, m. p. 138° . By hydrolysis, this gives an acid, which was not further investigated.

By the action of dry sodium methoxide on *as*-diphenyldichloroethylene, diphenylketenacetal was not obtained, but a complex reaction ensued with production of diphenylmethane, tolane, and methyl alcohol. Attempts to prepare the ortho-ester of diphenylacetic acid by the action of alcohol on ethyl diphenylimidoacetate were unsuccessful. *Ethyl diphenylimidoacetate*, $\text{CHPh}_2\cdot\text{C}(\text{NH})\cdot\text{OEt}$, was prepared by passing hydrogen chloride at -80° into a mixture of light petroleum, diphenylacetoneitrile and the calculated quantity of alcohol in an autoclave and allowing the mixture to remain at the ordinary temperature for a long time. Its *hydrochloride* has m. p. 128 – 130° , decomposing into diphenylacetamide and ethyl chloride.

By the action of diphenylketen on orthoformic ester at 60° , the acetal of *ethyl diphenylformylacetate*, $\text{CO}_2\text{Et}\cdot\text{CPh}_2\cdot\text{CH}(\text{OEt})_2$, is formed, m. p. 58° , a remarkably stable substance. It is not decomposed by alcoholic potassium hydroxide, but with warm concentrated hydrochloric acid it breaks up, giving diphenylacetic acid, ethyl chloride, and formic acid.

E. H. R.

Ketens. XLI. Methylene-carbonic Acid Derivatives [*Ketenacetals, etc.*]. H. STAUDINGER and P. MEYER (*Helv. Chim. Acta*, 1922, 5, 656–678).—From the analogies in the constitutions $\text{OC}(\text{OEt})_2$ and $\text{CR}_2\cdot\text{C}(\text{OEt})_2$, the ketenacetals (previous abstract) may be regarded as the normal esters of methylene-carbonic acid. Their derivatives, such as $\text{CR}_2\cdot\text{C}(\text{ONa})\cdot\text{OEt}$, are enolic forms of derivatives of acid esters. These are already known in the form of derivatives of ethyl malonate. In the present paper are described attempts to obtain derivatives of the types $\text{CR}_2\cdot\text{C}(\text{OM}')\cdot\text{OEt}$ and $\text{CR}_2\cdot\text{C}(\text{OM}')_2$, where M' is an alkali metal, most of the experiments being made with ethyl diphenylacetate. *Potassioxyethoxy-diphenylketen*, $\text{CPh}_2\cdot\text{C}(\text{OK})\cdot\text{OEt}$, was obtained best by treating ethyl diphenylacetate with potassamide in liquid ammonia. An additive product was first obtained which by heating in a vacuum at 100 – 120° lost ammonia. It was also prepared by treating the ester with potassium suspended in toluene, but was not isolated by this method. The salt is spontaneously oxidised by oxygen.

without, however, forming a stable peroxide. The oxidised salt is decomposed by water, giving benzophenone and benzilic acid. When alkylated with methyl iodide, the ester salt gives ethyl $\alpha\alpha$ -diphenylpropionate. Diphenylketen reacts with it to form tetraphenylacetone and tetraphenylallene, the production of which is difficult to explain.

The carboxylic acids show little tendency to form enol derivatives. Thus it was found impossible by heating sodium diphenylacetate or sodium isobutyrate with sodium methoxide to obtain the normal sodium salt derivative of diphenylketendiol. Sodium diphenylacetate showed some tendency to enolise under these conditions to form a yellow salt, but the best result was obtained by heating potassium diphenylacetate with potassamide in liquid ammonia, when dipotassoxydiphenylketen, $\text{CPh}_2\text{C(OK)}_2$, was obtained as a yellow precipitate. The yellow salt could not be crystallised. It was also obtained by the action of potassium on potassium diphenylacetate in liquid ammonia, and a similar salt was obtained from diphenyleneacetic acid, $\text{C}_6\text{H}_4\text{CH(CO}_2\text{H)}_2$, but not from salts

of acetic, isobutyric, succinic, or malonic acid. It is noteworthy that whilst ethyl malonate enolises more readily than ethyl diphenylacetate, in the case of the potassium salts the tendency to enolise is reversed. Dipotassoxydiphenylketen undergoes autoxidation in oxygen, forming an explosive peroxide. The peroxide, a colourless solid, is formed by absorption of two atoms of oxygen and appears to have a high molecular weight. When gently heated, it decomposes more or less explosively into benzophenone and potassium carbonate. When the potassium compound, suspended in toluene, is oxidised carefully with air, a monoxide is formed, probably having the structure $\text{O} \begin{smallmatrix} \text{CPh}_2 \\ | \\ \text{C(OK)}_2 \end{smallmatrix}$, which when

treated with acids or alkalis forms benzilic acid. Alkylation of dipotassoxydiphenylketen with methyl iodide gives potassium $\alpha\alpha$ -diphenylpropionate, whilst the more active methyl sulphate gives the corresponding methyl ester. These products of alkylation afford proof that when enolic compounds are alkylated the alkyl group becomes primarily attached to the carbon atom. If combination first occurred at the oxygen atom, a potassium enol derivative of the ester would be formed and a C-alkylated derivative would not be obtained.

The greater reactivity of the salts of ketendiol, which are coloured and autoxidisable, compared with the esters which are not, is paralleled by the greater reactivity of the salts of the polyhydroxy-benzenes such as pyrocatechol and pyrogallol as compared with their ethers.

E. H. R.

Alkali Salts of Benzil and the Benzilic Acid Transformation. H. STAUDINGER and A. BINKERT (*Helv. Chim. Acta*, 1922, 5, 703—710).—In a previous paper (preceding abstract) the difference between the reactivity, for instance the autoxidisability, of the polyhydroxybenzenes in the form of their alkyl derivatives and

of their sodium salts, was compared with the difference between the salts and esters derived from ketenacetals. The investigation is now extended to the salts of stilbenediol, $\text{OH}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{OH}$, which is isomeric with diphenylketendiol, $\text{Ph}_2\text{C}\cdot\text{C}(\text{OH})_2$. The potassium salts of stilbenediol are formed to some extent when benzoin is treated with potassamide in liquid ammonia, or by the reduction of benzil by potassium in liquid ammonia, but they are best obtained by reducing benzil with potassium in boiling benzene. The dipotassium salt is red and the monopotassium salt violet. The red salt is decomposed by water, giving benzoin; with acetic anhydride, it gives β -stilbene diacetate, probably with a little of the α -form, and with benzoyl chloride the corresponding *dibenzoate* in two probably stereoisomeric forms, m. p. 159° and $185\text{--}187^\circ$. The *dimethyl ether*, probably the α -form, has m. p. 127° . The monopotassium salt is to be regarded as a compound of the quinhydrone type, formed between one mol. of benzil and one of dipotassium salt, as in the annexed formula. Its deep colour $\text{Ph}\cdot\text{COK} \dots \text{O}\cdot\text{C}\cdot\text{Ph}$ supports this opinion, and also the fact that with acetic anhydride and benzoyl chloride $\text{Ph}\cdot\text{COK} \dots \text{O}\cdot\text{C}\cdot\text{Ph}$ it gives a mixture of benzil and of stilbenediol derivative. The dipotassium salt is autoxidisable, like the corresponding salt of diphenylketendiols; in the cold, potassium benzoate is formed, but in the warm a mixture of benzoic acid and benzoic acid. The former probably results from a peroxide, $\text{O}\cdot\text{CPh}\cdot\text{OK}$, the latter from a monoxide, $\text{O} < \begin{matrix} \text{CPh}\cdot\text{OK} \\ \text{CPh}\cdot\text{OK} \end{matrix}$. A suggested explanation of the benzoic acid transformation is as follows. The action of alkali on benzil leads first to an additive product, a pinacone, $\text{OK}\cdot\text{CPh}(\text{OH})\cdot\text{CPh}(\text{OH})\cdot\text{OK}$. This may lose water to form the above oxide, which then undergoes transformation, or the pinacone may change over directly, the transformation being a special case of the pinacone-pinacoline change. E. H. R.

isoCampholic Acid. H. RUPE and P. BRIELMANN (*Helv. Chim. Acta*, 1922, 5, 767—777).—Experiments were made to investigate more fully the *isocampholic acid* first prepared by Guerbet (A., 1895, i, 61) and if possible to determine its constitution. The material was obtained from the campholic acid prepared by heating camphor with potassium hydroxide at 280° in an iron autoclave, and was finally purified by converting it into the acid chloride and thence into the amide. The *chloride*, $\text{C}_{10}\text{H}_{17}\text{OCl}$, is a mobile liquid, b. p. $103^\circ/11\text{ mm.}$; the *amide* forms lustrous, white scales, m. p. 112° . The *isocampholic acid* prepared by hydrolysing the amide forms a pale yellow, mobile oil, b. p. $141^\circ/9\text{ mm.}$, d_4^{20} 0.9789, $[\alpha]_D^{20} +30.36^\circ$, $[\alpha]_D +26.26^\circ$ in benzene, $n=1.46061$. Ethyl *isocampholate* is a liquid with a peppermint-like odour, b. p. $103^\circ/12\text{ mm.}$, d_4^{20} 0.9426, $[\alpha]_D^{20} +26.64^\circ$, $n=1.44572$. The *amide* crystallises in fine, white needles or prisms, m. p. 119.5° , and the *p-toluidide* in needles, m. p. $133\text{--}134^\circ$. *isoCampholic acid* is formed slowly when campholic acid is heated with potassium hydroxide at 280° . By nitric acid it is oxidised to camphoric

acid. By bromination with bromine and phosphorus, *isocampholic* acid was converted into a *bromoisocampholic bromide*, a white solid which reacted with alcohol, giving ethyl *bromoisocampholate*, a white, mobile oil with an intense peppermint-like odour, b. p. 125.5°/8 mm. When boiled with methyl alcoholic potassium hydroxide, the *bromoisocampholic* ester was converted into an *unsaturated acid*, an odourless oil, b. p. 146—147°/8 mm., d_4^{20} 1.0374, $[\alpha]_D^{20} +15.88^\circ$. It forms a *silver* salt, fine, white needles, $C_{10}H_{15}O_2Ag$. The constitution of this acid was not elucidated. It is shown that *isocampholic* acid cannot be identical with dihydrocampholenic acid, as supposed by Mahle and Tiemann (A., 1900, i, 507) or with the dihydrocampholenic acid described by van Kregten (A., 1916, i, 480). It is suggested that it may have the constitution $CMe_2 \cdot CMe_2 > CH \cdot CO_2H$, being formed by intramolecular change $CH_2 \rightarrow CH_2$ from campholic acid.

E. H. R.

p-Dithiobenzoic Acid. SAMUEL SMILES and DOUGLAS CREESE HARRISON (T., 1922, 121, 2022—2026).

The Constitution of Vacciniin. HEINZ OHLE (*Biochem. Z.*, 1922, 131, 611—613).—Monoacetoneglucose was benzoylated in pyridine solution by benzoyl chloride in chloroform and gave ζ -benzoylmonoacetoneglucose identical with the acetone condensation product of vacciniin (A., 1918, i, 226). Monoacetoneglucose is converted by shaking with anhydrous copper sulphate in dry acetone into diacetoneglucose. This reaction fails with ζ -benzoylmonoacetoneglucose and thus determines the ζ -position for the benzoyl group in vacciniin. H. K.

The Chlorination and Bromination of the Toluic Acids and the Preparation of the Phthalaldehydic Acids. WILLIAM DAVIES and WILLIAM HENRY PERKIN, jun. (T., 1922, 121, 2202—2215).

Photo-reactions of the *trans*- and *cis*-Cinnamic Acids. HANS STOBBE and FRANZ KARL STEINBERGER (*Ber.*, 1922, 55, [B], 2225—2245; cf. de Jong, this vol., i, 339).—The authors' views on the polymerisation of the cinnamic acids under the influence of light coincide with those of de Jong in that α -truxillic acid is considered to be formed solely by the polymerisation of two molecules of *trans*-cinnamic acid, but differ with regard to the origin of β -truxinic acid. From the results of his experiments on the polymerisation of mixtures of *trans*- and *cis*-cinnamic acids, de Jong has drawn the conclusion that a molecule of β -truxinic acid is formed from a molecule of *cis*- and a molecule of *trans*-cinnamic acid. The author does not consider that the experimental evidence is conclusive, and is of the opinion that the whole process is represented accurately by the scheme β -truxinic acid \leftarrow *cis*-cinnamic acid (solid) \rightleftharpoons *trans*-cinnamic acid (solid) \rightarrow α -truxillic acid, according to which β -truxinic acid is derived solely from *cis*-cinnamic acid. Experimental evidence in favour of this view is now recorded.

Exposure of molten *allo*-cinnamic acid to the light of a quartz-mercury vapour lamp causes extensive isomerisation to *trans*-cinnamic acid, but does not result in the formation of truxillic or truxinic acids, its behaviour under these conditions resembling that which is observed in benzene solution (Stoermer, A., 1910, i, 114). The action is caused mainly by the rays of wave length, 270–320 μ , although those of shorter and greater length are active to a less extent.

The behaviour of pure *allo*- and *trans*-cinnamic acids and of mixtures of them when exposed to the light of the Uviol lamp and to sunlight, respectively, has been examined in detail. The isomerisation of the *cis*- to the *trans*-acid takes place in much the same manner with either source of light, but sunlight is far more effective than artificial light in causing polymerisation. This is due to the dissimilarity of the lights. The Uviol rays of long wave-length induce polymerisation, whereas those of short wave-length retard polymerisation and actually have a depolymerising effect on the truxinic and truxillic acids. The exposure of *cis*-cinnamic acid to sunlight leads invariably and generally preponderatingly to the production of β -truxinic acid; prolonged exposure causes isomerisation to the *trans*-acid and subsequent polymerisation to α -truxillic acid. *trans*-Cinnamic acid, on the other hand, is polymerised almost exclusively to α -truxillic acid. After protracted illumination, the formation of relatively small amounts of β -truxinic acid, in addition to much resinous matter, is observed, but the presence of *cis*-cinnamic acid could not be established. The addition of *trans*- to *cis*-cinnamic acid does not result in the increased production of β -truxinic acid. (The structure assigned to β -truxinic acid by de Jong (*loc. cit.*) is thus invalidated, but it is not yet possible to decide between the alternatives proposed by Stoermer and Scholtz [A., 1921, i, 180].)

trans-Cinnamic acid is polymerised to α -truxillic acid and autoxidised to benzaldehyde if its aqueous solution is exposed to light, particularly in the presence of a little hydrochloric acid. Under similar conditions, *cis*-cinnamic acid (m. p. 68°) gives β -truxinic acid and benzaldehyde; the yield of acid diminishes after protracted illumination particularly in the presence of hydrochloric acid, owing to pronounced autoxidation. Experiments with a mixture of the *cis*- and *trans*-acids show that the production of β -truxinic acid is independent of the presence of admixed *trans*-acid. It is remarkable that the *trans*-cinnamic acid formed by isomerisation is less readily polymerised than the acid introduced in powder form; the phenomenon is explained by a progressive change in the absorptive capacity of the illuminated crystals.

The conversion of prismatic, metastable β -*trans*-cinnamic acid by light into β -truxinic acid has been recorded by de Jong (*loc. cit.*). It is now shown that the latter acid is produced in relatively better yield when the β -cinnamic acid is exposed to light shortly after its recrystallisation than after the lapse of such an interval that its partial conversion into α -cinnamic acid has commenced and that β -cinnamic acid freshly precipitated from solutions of its

sodium salt gives exclusively β -truxinic acid, which is free from α -truxillic acid. A possible explanation of these observations is found in the suggestion that the highly reactive β -cinnamic acid is more readily isomerised than α -cinnamic acid to *allo*-cinnamic acid which is subsequently polymerised normally to β -truxinic acid. The authors do not consider that the difference in the behaviour towards light of α - and β -cinnamic acids necessarily proves their chemical isomerism; since the observations have been uniformly made with crystalline material and the power of absorbing light varies in anisotropic material according to the direction of the axis, it is possible that the two acids are to be regarded as two forms of a dimorphous cinnamic acid.

The influence of temperature on the photochemical polymerisation of *allocinnamic* acid has been examined by de Jong (*loc. cit.*), who, however, does not appear to have taken into consideration the importance of the melting of the acid at temperatures above 60° .

A convenient method for the preparation of *allocinnamic* acid by the partial hydrogenation of sodium phenylpropionate in the presence of palladised barium sulphate is described in detail. A modified process for the estimation of *cis*- and *trans*-cinnamic acids, α -truxinic and β -truxillic acids in mixtures containing the four substances is given (cf. de Jong, A., 1913, i, 384; Stoermer, A., 1919, i, 444).
H. W.

Preparation of *d*-Pimaric Acid of m. p. 212° . EDMUND KNECHT and EVA HIBBERT (*J. Soc. Dyers and Col.*, 1922, 38, 221—222).—*l*-Pimaric acid, of m. p. 161° and $\alpha_D -80^\circ$, when exposed to the air for prolonged periods, or when subjected to alkaline oxidation, is partly converted into the *d*-pimaric acid, $C_{20}H_{30}O_2$, m. p. 212° and $\alpha_D +62.5^\circ$, described by Laurent, Vesterberg, and others. The reaction is conveniently carried out by keeping overnight a mixture of a dilute solution of the sodium salt of *l*-pimaric acid (25 grams) and 400 c.c. of sodium hypochlorite solution (75 grams available chlorine per litre). The crystalline precipitate which forms is dissolved in boiling water and decomposed with sulphuric acid. By recrystallising the liberated acid from alcohol, it is obtained in a pure condition in a yield of about 10%. *d*-Pimaric acid, m. p. 161° , $\alpha_D +80^\circ$, behaves in a similar way to the *l*-acid.
G. F. M.

Keto-enolic Equilibria and Claisen's Rule. W. DIECKMANN (*Ber.*, 1922, 55, [B], 2470—2491).—As the result of an extended study of a large variety of desmotropic substances, the author draws the conclusion that Claisen's rule has only a very limited applicability and that the tendency towards enolisation of a substance and its acidity are influenced in a complex manner by other constitutive influences which are not yet distinctly defined. Meyer's bromine titration method has been found to be very generally applicable and the relationship $K=EL$ (in which E is the constant of enolisation, K the equilibrium constant, and L the enolising action of the solvent) has been confirmed in the great majority of cases (cf. K. H. Meyer, A., 1912, i, 940).

It has been considered previously by Meyer that the enolising power of the carbomethoxy- is inferior to that of the carbethoxy-group, although there is no difference in their acidity. The enolic constants of methyl and ethyl acetoacetates are now found to be identical as are those of the corresponding benzoylacetates. The differences in enol content of the equilibrium esters is explicable if they are regarded as solutions of the enolic ester in the ketonic ester, and it is remembered that the ketonic ethyl ester has a higher enolising power than the corresponding methyl compound. This hypothesis is supported by the observation that ethyl acetate has a higher desmotropic constant than methyl acetate and that these constants are related to one another in the same ratio as the equilibrium constants of ethyl and methyl acetoacetates.

According to Meyer's observations (A., 1914, ii, 351), the behaviour of unsubstituted diacylmethanes is in accordance with Claisen's rule. This is not the case with the monoalkyldiacylmethanes, $R\cdot CO\cdot CHMe\cdot COR'$. In equilibrium in alcoholic solution, methylacetylacetone contains about 34% of enol, methylbenzoylacetone 7%, and methyl dibenzoylacetone only about 0.3% of enol. The enolic constant diminishes from methylacetylacetone ($E=ca. 3.9$) to methylbenzoylacetone ($E=0.06$) and further to methyl dibenzoylmethane ($E=ca. 0.02$). A similar deviation from Claisen's rule is observed among triacylmethanes, the enolic constant of tribenzoylmethane ($E=ca. 10$) being very appreciably lower than that of dibenzoylacetylmethane ($E=ca. 78$).

Cyclic β -ketonic carboxylic esters do not conform to Claisen's rule. Such esters of the penta- and hexa-methylene series are distinguished from their aliphatic analogues, the monoalkyl-acetoacetic esters, by greater acidity, as demonstrated by their solubility in alkali, and power of forming copper salts when treated with copper acetate. The acidity is considerably more pronounced in the cyclopentane than in the cyclohexane series. It is now shown that the more strongly acidic ethyl cyclopentane-2-one-1-carboxylate contains only 4.5% of enol in its equilibrium mixture, and that this value only slightly exceeds that of its aliphatic analogue, ethyl ethylacetoacetate (3%), whereas ethyl cyclohexane-2-one-1-carboxylate contains 76% of enol. This remarkable difference persists in its equilibrium mixtures in solution. The enolic constant of ethyl cyclopentane-2-one-1-carboxylate ($E=ca. 0.5$) is only slightly greater than that of ethyl ethylacetoacetate ($E=0.23$) and very much less than that of ethyl cyclohexane-2-one-1-carboxylate ($E=ca. 12$). The tendency towards enolisation appears to be conditioned in these cases by constitutive influences other than acidity, and is presumably connected with the condition of strain in the cyclopentane and cyclohexane rings. To gain further insight into these relationships, other ring systems have been studied. Ethyl cycloheptane-2-one-1-carboxylate has $E=ca. 1.2$ and similar acidity to the cyclohexanone ester, whereas ethyl camphorcarboxylate, which contains a five- and a six-membered ring, has a remarkably lower enolic constant ($E=0.04$) and very slight acidity.

In contrast to the tendency towards enolisation of ethyl β -cyclohexanonecarboxylate, it is remarkable that ethyl cyclopentane-2:3-dione-1:4-dicarboxylate and its 5-phenyl derivative are stable in the dienolic form in the solid state and in solution; this is also true for ethyl cyclopentane-2:3-dione-1-carboxylate and its 5-phenyl compound. The marked increase in tendency towards enolisation is explained in accordance with Claisen's rule by the great increase in acidity due to the presence of the keto-group in the α -position.

The great dependence of tendency towards enolisation and acidity on cyclic structure and constitutive influences is illustrated by the behaviour of benzo-derivatives of cyclopentanonecarboxylic esters. Ethyl α -hydriindone- β -carboxylate, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{CH}_2 \end{smallmatrix} \text{CH-CO}_2\text{Et}$,

has the enolic constant $E = ca. 2.4$, and is a relatively weak acid which cannot be titrated with alkali in aqueous-alcoholic solution,

whereas ethyl β -hydriindone- α -carboxylate, $C_6H_4 \begin{smallmatrix} \text{CH}-(CO_2Et) \\ \text{CH}_2 \end{smallmatrix} \text{CO}$,

has a high enolic constant and such marked acidity that it can be titrated with alkali in aqueous-alcoholic solution as a monobasic acid. The acyclic analogues of the esters exhibit greatly diminished acidity and considerably smaller constants of enolisation. Ethyl benzylbenzoylacetate has $E = ca. 0.3$, whereas ethyl α -diphenylacetate has $E = 3.6$.

Meyer indirect and direct bromine titration methods are smoothly applicable to unsubstituted 1:3-dicarbonyl compounds, $R\cdot CO\cdot CH_2\cdot CO\cdot R'$. The monoalkyl derivatives of these compounds cannot in many cases be so treated. The indirect method is unsuitable, since the bromo-derivatives do not react smoothly and quantitatively with hydriodic acid; the direct method is difficult, owing to the uncertainty in recognition of the end-point, particularly in dilute solution and in the presence of small amounts of material. Under these conditions, it is frequently advisable to modify the process by adding a known excess of bromine followed by potassium iodide and immediately titrating the liberated iodine.

The following substances have been prepared incidentally. Methyl dibenzoylmethane, $COPh\cdot CHMe\cdot COPh$, from dibenzoylmethane, sodium ethoxide, and methyl iodide in absolute ethyl alcoholic solution, m. p. about 85° (cf. Beyme, *Disa.*, Leipzig, 1900), and the corresponding enolic form, colourless leaflets, m. p. 110° ; ethyl cyclopentane-2:3-dione-1-carboxylatediphenylhydrazone, yellow crystals, m. p. 138° ; ethyl 5-phenylcyclopentane-2:3-dione-1-carboxylatediphenylhydrazone, yellow crystals, m. p. 181° ; ethyl methylquinoxalinocyclopentane-2:3-dione-1-carboxylate (from the parent ester and o-tolylenediamine), yellow crystals, m. p. 123° ; ethyl 2-hydriindone-3-carboxylate (enolic form), $C_6H_4 \begin{smallmatrix} \text{C}(CO_2Et) \\ \text{CH}_2 \end{smallmatrix} \text{C}\cdot OH$, colourless crystals, m. p. $68-69^\circ$. H. W.

Ethyl Esters of p - β -Hydroxyethylaminobenzoic Acid and of p -Bis- β -hydroxyethylaminobenzoic Acid. J. ALTWEGG and J. LANDRIVON (U.S. Pat. 1418900).—Ethyl p - β -hydroxyethylamino-

benzoate, colourless crystals, m. p. 63—64°, b. p. 213—214°/4 mm., is obtained by distillation under reduced pressure after heating a mixture of equimolecular proportions of ethyl *p*-aminobenzoate and ethylene oxide at 50° for several hours. *Ethyl p-bis-β-hydroxy-ethylaminobenzoate*, white lamellæ, m. p. 94°, b. p. 246°/3—4 mm., is similarly obtained from 2 mols. of ethylene oxide with the addition of small quantities of water and alcohol. The compounds are adapted for use as local anæsthetics. CHEMICAL ABSTRACTS.

The Reduction of Substituted Salicylic Acids. HUGO WEIL, MAX TRAUN, and SIGISMOND MARCEL (*Ber.*, 1922, 55, [B], 2664—2674; cf. A., 1908, i, 800; this vol., i, 139).—Reduction of 2:3-, 2:5-, and 2:4-hydroxymethylbenzoic acids by sodium amalgam in the presence of boric acid and neutral sodium sulphite solution gives the corresponding aldehydes in a yield of about 33%. 5-Chlorosalicylic acid, m. p. 167.5°, prepared from 5-aminosalicylic acid hydrochloride, is similarly reduced to 5-chlorosalicylaldehyde, m. p. 99.5° (yield 20%); 5-bromosalicylic acid gives 5-bromosalicylaldehyde, m. p. 104—105° (yield 12.5%), and 3:5-dibromosalicylic acid yields 3:5-dibromosalicylaldehyde, m. p. 85° (yield 5%). Quinol- and pyrogallol-carboxylic acids cannot be reduced in this manner, whereas resorcylic acid gives resorcyaldehyde, large, yellow crystals, m. p. 134—135°. 5-Aminosalicylic acid hydrochloride, prepared by the reduction of 5-nitrosalicylic acid with zinc dust and dilute hydrochloric acid, suffers loss of the amino-group when reduced and appears to be converted into *hexahydrosalicylaldehyde*, which cannot be isolated. With phenylhydrazine, it gives a very unstable compound, straw-yellow leaflets, m. p. 151° (which is examined more fully in the form of its more stable *hydrochloride*, a crystalline substance, m. p. 137°); it appears to be an osazone-like substance formed presumably owing to the presence of a hydroxyl group in the ortho-position to the aldehydic group on the reduced nucleus. Stable, oxygen-free derivatives of the aldehyde are obtained with *p*-bromo- and *p*-nitro-phenylhydrazines, but neither compound appears to be perfectly homogeneous.

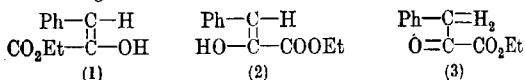
[With SIGISMOND MARCEL.]—Further examination of the reduction of 5-aminosalicylic acid has shown that 5-aminosalicylaldehyde (see later) may be produced in yield which may amount to 16%. For its isolation, the reduction is effected in the usual manner and the solution is boiled under a reflux condenser with sulphuric acid until the sulphur dioxide is removed. The solution is treated with sodium acetate until it is no longer acid towards Congo-red, and preserved during twenty-four hours in an atmosphere of carbon dioxide. 5-Aminosalicylaldehyde separates as a red precipitate which is precipitated by phenylhydrazine as the compound $C_{19}H_{24}N_4$, almost colourless, unstable crystals, m. p. 155°; the corresponding *di-p-bromophenylhydrazone* forms almost colourless crystals, m. p. 204°. The residual solution after the separation of 5-aminosalicylaldehyde is continuously extracted with ether, whereby pimelaldehyde, $[CH_2]_5(CHO)_2$ (Braun and Danziger, A.,

1913, i, 243) [identified as the *disemicarbazone*, a colourless, crystalline powder, m. p. 244° (decomp.)], is obtained.

For comparative purposes, 5-aminosalicylaldehyde is prepared in the following manner. Salicylaldehyde is dissolved in dilute aqueous sodium hydroxide solution and mixed with a diazotised solution of sulphanilic acid, when 5-benzeneazosalicylaldehyde-4'-sulphonic acid is produced. This is dissolved in water and reduced at 60–70° by hydrogen sulphide in the presence of sodium carbonate; 5-aminosalicylaldehyde separates completely in the course of two or three days. It is analysed in the form of its red hydrochloride, $C_7H_7O_2N.HCl$. It is further characterised by conversion into its phenylhydrazone [which exists in two modifications, m. p. 263° (decomp.), and pale yellow flocks, m. p. 164–165° (decomp.), respectively], and semicarbazone, m. p. above 300° (decomp.).

H. W.

Ethyl Phenylpyruvate. H. GAULT and R. WEICK (*Bull. Soc. chim.*, 1922, [iv], 31, 867–897; cf. Bougault and Hemmerlé, A., 1915, i, 78).—A third isomeride of ethyl phenylpyruvate was obtained as a white solid by the action of a solution of sodium acetate or copper acetate for forty-eight hours at 0° on the liquid isomeride previously described. The three forms— α , white needles, m. p. 52°; β , mobile, yellow liquid, b. p. 152°/15 mm., and γ , white solid, m. p. 79°—were studied with regard to their mutual transformations, and it was found that the α - and γ -esters are converted into the β -form by slow distillation under reduced pressure, whilst treatment with a saturated solution of sodium carbonate transforms both β - and γ -esters into the α -form. Treatment with acetate (see above) changes the β - into the γ -isomeride, but no direct transformation from α to γ was effected. An examination of the three substances with the view of determining their constitutions leads to the conclusion that, in addition to the keto-enolic isomerism, the enolic form exhibits stereoisomerism and the formulæ assigned are



(1) and (2) represent the α - and β -esters, the γ -ester being of the ketonic type.

H. J. E.

The Solubility of the Aldehydobenzoic Acids. NEVIL VINCENT SIDGWICK and HERBERT CLAYTON (T., 1922, 121, 2263–2267).

Cinnamoylformic Acids. GUSTAV HELLER, HILDE LAUTH, and ARNOLD BUCHWALDT (*Ber.*, 1922, 55, [B], 2679).—*m*- and *p*-Nitrocinnamoylformic acids have been described by Ciusa (A., 1919, i, 402). They were, however, obtained by condensation in an alkaline medium, whereas the authors (this vol., i, 348) worked in acid solution, in which the different ability of the three nitroaldehydes to undergo condensation is manifest.

H. W.

The Friedel-Crafts' Reaction with Phthalic Anhydride.

T. C. McMULLEN (*J. Amer. Chem. Soc.*, 1922, 44, 2055—2060; cf. Heller, A., 1908, i, 994; 1912, i, 357; McMullen, this vol., i, 140; Stephens, this vol., i, 141; Rubidge and Qua, A., 1914, i, 539; Lawrence and Oddy, this vol., i, 453).—Phthalic anhydride and aluminium chloride dissolve in benzene to form a clear solution from which a viscous precipitate separates subsequently with the evolution of hydrogen chloride. The precipitate yields *o*-benzoylbenzoic acid when hydrolysed.

The clear solution of phthalic anhydride and aluminium chloride in benzene is transformed when heated with naphthalene into a mixture of benzoylbenzoic acid (60%), naphthoylbenzoic acid (35%), and phenylnaphthylphthalide (5%). If the "clear solution" is treated with ether, a heavy, pale brown liquid is precipitated which yields exclusively *o*-benzoylbenzoic acid on treatment with dilute hydrochloric acid and does not give naphthoylbenzoic acid when heated with naphthalene. The "insoluble intermediate compound," which appears to have the composition $C_{14}H_8O_3Al_2Cl_5$, is prepared conveniently by slowly heating aluminium chloride, benzene, and phthalic anhydride to 50°; it is transformed by acetic anhydride and toluene into a little benzoylbenzoic acid and much phenyl-*p*-tolylphthalide, m. p. 106°, by acetic anhydride and naphthalene into a mixture of phenyl- β -naphthylphthalide, m. p. 153—154°, and phenyl- α -naphthylphthalide, m. p. 227—228°, and by anthracene into a mixture of *o*-benzoylbenzoic acid and two substances, yellowish-white crystals, m. p. 171—173°, and brownish-white crystals, m. p. 280—283°, which are probably phenylanthrlylphthalides, but could not be identified more completely (a non-crystalline gum is also produced in considerable quantity). The intermediate compound from toluene reacts slowly with benzene and acetic anhydride, yielding *p*-toluoylbenzoic acid together with a relatively small amount of phenyl-*p*-tolylphthalide. The intermediate compound from naphthalene reacts sluggishly under similar conditions, but it is not possible to separate any phthalide from the viscous product of the reaction.

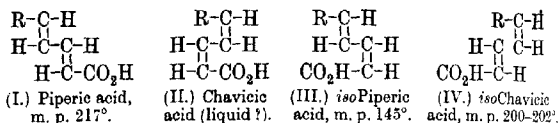
α -Naphthoylbenzoic acid, m. p. 176°, is prepared according to the method of Heller and Schülke (A., 1908, i, 994); considerable amounts of β -naphthoylbenzoic acid (cf. Pickles and Weizman, P., 1904, 20, 201), needles, m. p. 165°, are simultaneously produced. The α -acid is converted by acetic anhydride into the corresponding *acetyl* compound, m. p. 141°, which is transformed by benzene and aluminium chloride into phenyl- α -naphthylphthalide (see above). Similarly, the *acetyl* derivative of β -naphthoylbenzoic acid, m. p. 140°, is converted into phenyl- β -naphthylphthalide.

Phenyl- α -naphthylphthalide is reduced by zinc dust in the presence of potassium hydroxide solution to 2-phenyl- α -naphthylmethylbenzoic acid, m. p. 189°, the *potassium, silver, and barium* salts of which are described. The latter salt is transformed when heated with barium hydroxide into diphenyl- α -naphthylmethane, m. p. 152° (cf. Acree, A., 1904, i, 315). Similarly, phenyl- β -naph-

thylphthalide is reduced to *phenyl-2-β-naphthylmethylbenzoic acid*, m. p. 150° (m. p. 76–77° when containing benzene of crystallisation); the *silver* salt is analysed. The *barium* salt is converted by barium hydroxide at about 225° into *diphenyl-β-naphthylmethane*, m. p. 73–74°.

H. W.

Natural and Artificial Pepper-substances. II. The Chavicine of Pepper-resin, the Primarily Active Constituent of Black Pepper. ERWIN OTT and FRITZ EICHLER [with OTTO LÜDEMANN and HEINRICH HEIMANN] (*Ber.*, 1922, 55, [B], 2653–2663; cf. Ott and Zimmermann, this vol., i, 137).—The active constituent of black pepper has been isolated previously by Buchheim, who designated it chavicine and, in an incompletely purified material, identified the presence of piperidine and a resin acid, chavicie acid, which was not further identified. Re-examination of purified pepper-resin has shown that it very closely resembles piperine, and has established its nature as a piperide. It is hydrolysed by alkali hydroxide with extreme difficulty, and the acid which is formed differs so widely from chavicie acid in its properties that the conclusion is drawn that it has suffered isomerisation during the change. In its general behaviour, the new *isochavicie* acid is very closely allied to piperic acid, from which it differs somewhat in colour and melting point, but is mainly distinguished by its completely amorphous nature. For the four acids of this series, the possible formulæ are shown in the scheme, in which R represents the piperonyl radicle:



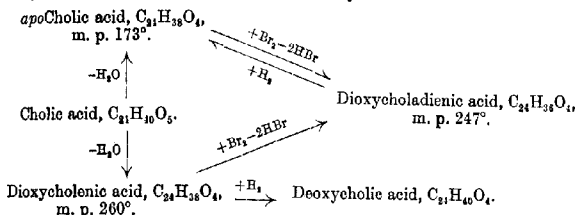
The allocation of formula I to piperic acid is justified by a review of the literature on this compound; the syntheses of *isopiperic* acid is recorded in the present communication, and its method of preparation leaves no doubt as to its configuration. The high melting point and general resemblance of *isochavicie* to piperic acid prove it to be a *trans*-acid, thus leaving formula II for chavicie acid.

Finely divided *Piper nigrum* Singapore is extracted with boiling rectified spirit and the solvent removed from the extract, leaving a solid, sticky residue which is extracted with ether until the solution is no longer coloured. The residue consists essentially of piperine. The ethereal solution is agitated with potassium hydroxide (10%) and washed with water; after removal of the ether, the residue is subjected to a very protracted distillation with steam to remove essential oils. The non-volatile portion is repeatedly treated with ether, and the solutions are cooled, thus causing the separation of piperine. The ethereal solution is evaporated, the residue extracted with light petroleum, and the undissolved matter decolorised by animal charcoal in alcoholic solution, after

complete removal of the solvent, whereby pepper-resin is obtained as a dark brown, transparent, very viscous mass; the material thus isolated is not quite homogeneous since in addition to chavicine it contains not inconsiderable amounts of wax and possibly also of chlorophyll. The hydrolysis of pepper-resin with alcoholic sodium hydroxide solution leads to the formation of piperidine and *isochavicine acid*, a yellow, amorphous substance, m. p. 200—202°. It is readily reduced by hydrogen in alcoholic solution and in the presence of palladised animal charcoal to tetrahydropiperic acid.

[With HEINRICH HEIMANN.]—*isoPiperic acid*, microscopic crystals, m. p. 145°, is prepared in poor yield by heating piperonylenemalonie acid at about 190° in the presence of quinoline. H. W.

Unsaturated Bile Acids. III. The Relationships of apo-Cholic Acid, Dioxycholenic Acid [m. p. 260°], and Cholic Acid to Deoxycholic Acid. F. BOEDECKER and H. VOLK (*Ber.*, 1922, 55, [B], 2302—2309; cf. A., 1920, i, 848; 1921, i, 865).—Further investigation of the unsaturated bile acids has shown that they are inter-related as indicated in the scheme:



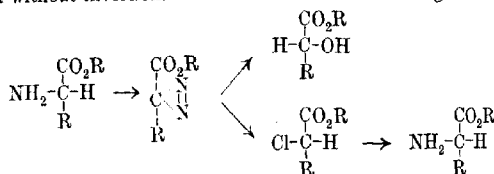
Dioxycholadienic acid, short rods, m. p. 245—247° (slight decomp.), $[\alpha]_D^{20} +20.3^\circ$ in absolute ethyl alcoholic solution, is prepared by the gradual addition of bromine to a solution of the additive compound of *apocholic* and glacial acetic acids in methyl alcohol at -10° and subsequent treatment of the product with water; it is obtained in somewhat better yield and by an analogous process from *dioxycholenic acid*, m. p. 260°. Its *alkali* salts are soluble in water. The *magnesium* and *barium* salts are obtained as oily precipitates which become crystalline when warmed. The *silver* salt crystallises in small, slender needles. The *methyl* ester, prepared by means of diazomethane, has m. p. 85° after softening at 79°. *Dioxycholadienic acid* absorbs one molecular proportion of hydrogen in glacial acetic acid in the presence of palladium black, the product formed appearing to be identical with *apocholic acid* as judged from the similarity of the acids themselves, their additive compounds with glacial acetic acid, xylene, and camphor, respectively, and their methyl esters; a divergence is noted, however, in the specific rotations, the additive compounds of glacial acetic acid, and the reduction products of *dioxycholadienic acid* from *apocholic* and *dioxycholenic acids* having $[\alpha]_D^{20} +55.9^\circ$ and $[\alpha]_D^{20} +52.04^\circ$ in alcoholic solution, whereas *apocholic acid* has $[\alpha]_D^{20} +45.35^\circ$ under similar conditions. The *dioxycholadienic*

acid prepared from this acid by addition of bromine and subsequent elimination of hydrogen bromide is identical with that prepared from apocholic acid except as regards specific rotation.

Dioxycholenic acid, m. p. 260° , is reduced by hydrogen in glacial acetic acid solution in the presence of palladium black to deoxycholic acid.

H. W.

Ethyl Benzylidenechitosamate and Ethyl Diazobenzylidene-glucosate (Mannonate). P. A. LEVENE (*J. Biol. Chem.*, 1922, **53**, 449–461).—When the diazo-group in ethyl diazobenzylidene-glucosamate (A., 1915, i, 786) is hydrolysed or replaced by hydrogen chloride or bromide, a single substance, and not a pair of epimerides, results in each case. In the former process, however, the direction of the rotation of the product is opposite to that of chitosamic acid, whereas it is the same in the products from the two latter processes. Further, conversion of the chloro-derivative into chitosamic acid (α -aminomannonic acid) takes place without change in the direction of the rotation and without the formation of epimerides. Assuming that, in these compounds, the configuration of the α -carbon atom determines the sign of the rotation of the acid, it appears that chitosamic acid undergoes the Walden inversion when deaminised through the diazo-compound (as it does when directly deaminised), whilst the diazo-compound can be reconverted through the chloro-derivative into the amino-acid without inversion. This is shown in the following scheme:



Ethyl benzylidenechitosamate [glucosamate] hydrochloride has m. p. 200° (uncorr.) and $[\alpha]_D^{20} -30^{\circ}$. By treatment with sodium hydroxide it is converted partly into *ethyl benzylidenechitosamate*, $\text{C}_{15}\text{H}_{21}\text{O}_6\text{N}$, m. p. 120° (corr.), $[\alpha]_D^{20} -50^{\circ}$ (in methyl alcoholic solution), and partly into *benzylidenechitosamic acid*, $\text{C}_{13}\text{H}_{17}\text{O}_6\text{N}$, m. p. 230° (uncorr.), $[\alpha]_D^{20} -28^{\circ}$ in aqueous solution. When boiled in acetone solution, ethyl benzylidenechitosamate yields *ethyl benzylideneacetonechitosamate*, $\text{C}_{18}\text{H}_{25}\text{O}_6\text{N}$, m. p. 128° , $[\alpha]_D^{20} -70^{\circ}$, which is readily reconverted into the hydrochloride of the former substance by treatment with ethereal hydrogen chloride in methyl alcoholic solution. Ethyl diazobenzylidene-glucosamate has $[\alpha]_D^{20} -50^{\circ}$, and when hydrolysed yields different products according to the conditions. When the reaction is carried out in organic solvents containing only a small proportion of water, ethyl α -anhydrogluconate is apparently produced, for the product yields *mesotartaric acid* on oxidation with nitric acid. Hydrolysis with dilute acetic acid, however, appears to yield ethyl gluconate or ethyl α -anhydrogluconate, since in this case either saccharic or

anhydrosaccharic acid is formed on oxidation. Treatment of the diazo-compound with hydrobromic acid in ethereal solution gives *ethyl β-bromobenzylidenemannonate*, $C_{15}H_{19}O_6Br$, m. p. 119° (corr.), $[\alpha]_D^{20} -33^\circ$, which is converted by treatment with ammonia into either *ethyl benzylidene-αβ-anhydromannonate*, $C_{15}H_{18}O_6$, $[\alpha]_D^{20} -73.3^\circ$, or the corresponding *amide*, $C_{15}H_{15}O_5N$, m. p. 230°, $[\alpha]_D^{20} +65^\circ$ according to the conditions. Reduction of the last-mentioned ester with hydrogen in the presence of colloidal palladium gives *ethyl benzylidenedeoxygluconate* (mannonate), $C_{15}H_{20}O_6$, m. p. 126° (corr.), $[\alpha]_D^{20} -26^\circ$. *Ethyl α-chlorobenzylidenegluconate*, $C_{15}H_{19}O_6Cl$, m. p. 127°, $[\alpha]_D^{20} -20^\circ$, and the corresponding *amide*, $C_{15}H_{16}O_5NCl$, m. p. 197° (corr.), $[\alpha]_D^{20} -23^\circ$, have also been prepared; the former is converted into chitosamic acid by treatment with ammonia and subsequent hydrolysis.

E. S.

Benzaldehyde-Copper and the Heterogeneous Rate of Formation of this Substance. AUGUST L. BERNOULLI and FRITZ SCHAAF (*Helv. Chim. Acta*, 1922, **5**, 721—731).—When a dilute solution of benzaldehyde in a solvent such as toluene, *m*-xylene, benzene, chlorobenzene, ethyl acetate, etc., is in contact with metallic copper, the metal dissolves forming an intense green solution. The rate of solution depends on the solvent, the benzaldehyde concentration, the temperature, and the surface area of copper exposed. The "specific solution velocity," v (the weight of copper dissolved per minute divided by the square root of the surface area of the copper in $cm.^2$), is a constant for a given solvent at a given concentration and temperature. The values of v for a series of different solvents at similar concentrations of benzaldehyde follow the same order as the value of the fluidity of the solvent. With toluene as solvent, the maximum rate of solution is reached with 16% benzaldehyde, when $v \times 10^7 = 254.2$ at 50°, whilst in benzene the maximum, $v \times 10^7 = 92.54$, is at a benzaldehyde concentration of 14% by volume. The most favourable concentration appears to be determined by the fluidity of the solution. In a 10% solution of benzaldehyde in toluene the value of $v \times 10^7$ increases from 21.4 at 25° to 758.8 at 105°. Pure benzaldehyde has no solvent action. Of substituted benzaldehydes, *p*-tolualdehyde and *p*-chlorobenzaldehyde behave similarly to benzaldehyde in toluene solution, whilst *p*-nitrobenzaldehyde has no solvent action on copper. The copper compound of benzaldehyde crystallises from toluene solution in green crystals having the composition $(C_6H_5 \cdot CHO)_2Cu$. The crystals are remarkably stable, being unattacked by water, alkalis, or dilute hydrochloric acid. With dilute nitric acid, benzoic acid and copper nitrate are formed. The crystals are also formed when benzylidene chloride is heated with copper in presence of a little sodium carbonate solution. The constitution of the substance is at present uncertain. Cupric oxide and sulphide also dissolve in benzaldehyde and toluene, forming a green solution. Of other metals, lead behaves in the same way as copper, forming a yellowish-brown solution, zinc gives a greenish-brown, silver a brownish-black, magnesium a

yellowish-brown, and cobalt a brown solution. Nickel, iron, and aluminium do not dissolve.

E. H. R.

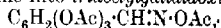
Gallaldehyde and its Derivatives. KARL W. ROSENMUND and E. PFANNKUCH (*Ber.*, 1922, 55, [B], 2357—2372).—The synthetic preparation of pure gallaldehyde has been achieved, and a number of its derivatives have been prepared. Considerable experimental difficulties are encountered owing to the sensitiveness of the aldehyde towards chemical reagents and to the physical characteristics of its derivatives. Attempts to circumvent these drawbacks by using the acylated aldehydes were prevented by the lack of activity of these substances.

Triacetyl-gallaldehyde, m. p. 107—108°, is prepared in good yield by the catalytic reduction of triacetyl-galloyl chloride according to the method of Rosenmund and Zetzsche (*A.*, 1918, i, 300), the purity of the materials being a very essential condition for success. The entrance of the acetyl groups inhibits almost completely the activity of the aldehyde complex; the only derivative obtainable is the *p*-nitrophenylhydrazone, yellow, rhombic plates or long needles, m. p. 207—208° (slight decomp.) when rapidly heated. It is hydrolysed by a boiling alcoholic solution of potassium acetate to gallaldehyde. Tribenzoyl-gallaldehyde, from gallaldehyde and benzoyl chloride by the Schotten-Baumann method, could only be obtained as a viscous, yellowish-brown mass which is identified as the *p*-nitrophenylhydrazone, indistinct, yellow crystals, m. p. 232—233° (decomp.) when placed in a bath pre-heated to 200°.

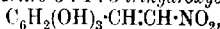
According to previous investigators, gallaldehyde is a stronger acid than acetic acid. This is not confirmed by observations on the electrical conductivity of its aqueous solutions, but the substance appears to be twice as strongly acid as pyrogallol.

Triacetyl-gallaldehyde diacetate, $C_6H_2(OAc)_3 \cdot CH(OAc)_2$, leaflets, m. p. 166°, is prepared by the action of acetic anhydride on gallaldehyde in the presence of pyridine.

Gallaldoxime, $C_6H_2(OH)_3 \cdot CH:N \cdot OH \cdot H_2O$, crystallises in rectangular plates, decomp. (anhydrous), 195—200° after darkening at about 160°. It is converted by cautious treatment with acetic anhydride and pyridine into triacetyl-gallaldoxime acetate,



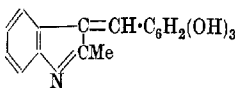
m. p. 126—127°. ω -Nitro-3:4:5-trihydroxystyrene,



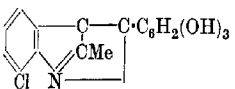
reddish-yellow needles, decomp. 180—185° after incipient decomposition at about 160°, is prepared by the action of nitromethane on gallaldehyde in the presence of methylamine, and is transformed by acetic anhydride and pyridine into ω -nitro-3:4:5-triacetoxy-styrene, colourless needles, m. p. 183° after previous darkening (ω -nitro-*p*-acetoxy-styrene, long, pale yellow needles, m. p. 163°, and ω -nitro-3:4-diacetoxy-styrene, pale yellow needles, m. p. 127°, are prepared similarly). Reduction of gallaldoxime by hydrogen in the presence of palladised barium sulphate gives mainly digallylamine, $NH \cdot [CH_2 \cdot C_6H_2(OH)_3]_2$, which could not be isolated in the pure condition; the corresponding hydrochloride, m. p. 208—210°,

and *picrate*, long, yellow needles, incipient decomp. 150—153°, are described. Triacetyl-gallaldoxime acetate, on the other hand, is reduced under similar conditions to triacetyl-gallylamine, which is isolated in the form of its *hydrochloride*, needles, m. p. 196—197° (decomp.). The latter is hydrolysed by dilute aqueous hydrochloric acid to *gallylamine hydrochloride*, m. p. 225—226° (decomp.), from which, however, free gallylamine could not be isolated.

Gallaldehyde reacts with methylketol in the presence of a saturated solution of hydrogen chloride in alcohol to form 3:4:5-trihydroxy-phenyl-2'-methyl-3'-indolydenemethane (annexed formula), the *hydrochloride* of which forms yellowish-red needles, decomp. about 170° after darkening at 140°. The salt is converted into the corresponding *dye* (annexed formula) by chloranil. When condensed with indoxyllic acid, gallaldehyde gives the compound,



decomp. about 170° after



brownish-red leaflets, m. p. 110—115° (decomp.) when rapidly heated.

Triacetyl-gallaldehyde is not reduced by hydrogen in the presence of palladium or spongy platinum; under similar conditions, gallaldehyde readily absorbs hydrogen, giving a more or less brown, amorphous mass which could not be purified, and, as judged from the molecular weight of its *acetate*, a pale yellow, amorphous powder, m. p. about 183—185°, is formed by the association of at least six molecules of the simple aldehyde.

Gallaldehydecyanohydrin, brownish-yellow, crystalline nodules, decomp. about 150—160° when very rapidly heated, is prepared by the addition of anhydrous hydrocyanic acid and a drop of concentrated potassium cyanide solution to gallaldehyde covered with alcohol. It is converted by acetic anhydride and pyridine into *tetra-acetyl-gallaldehydecyanohydrin*, $C_6H_2(OAc)_3 \cdot CH(OAc) \cdot CN$, colourless crystals, m. p. 135°.

Triacetylprotocatechualdehydecyanohydrin,
 $C_6H_3(OAc)_2 \cdot CH(OAc) \cdot CN$,
 has m. p. 112°.

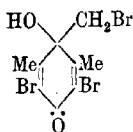
H. W.

2-Hydroxy-4:6-dimethylbenzaldehyde, Hemellitenol, and *iso-ψ*-Cumenol. K. VON AUWERS and K. SAURWEIN (*Ber.*, 1922, 55, [B], 2372—2389).—In continuation of their investigations on the oxidation of meta-substituted *o*-aminophenols (Auwers, Borsche, and Weller, *A.*, 1921, i, 571), the authors have prepared hemellitenol [3:4:5-trimethylphenol] and *iso-ψ*-cumenol [3:5:6-trimethylphenol]. Since these compounds have been difficultly accessible previously and consequently but little examined, they have been subjected to examination in several different directions.

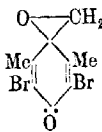
The initial material is *s.m*-xlenol which is converted by hydrocyanic acid and aluminium chloride according to Gattermann's method into a mixture of 2-hydroxy-4:6-dimethylbenzaldehyde

and 4-hydroxy-2 : 6-dimethylbenzaldehyde. The production of the *o*-hydroxyaldehyde appears to be contrary to Gattermann's rule, but is possibly attributable to the presence of moisture, since, on one occasion, the accidental presence of a relatively large quantity of water increased the yield of the substance from 8—12% to about 25%. In agreement with the observations of Steinich (A., 1916, i, 36), 2-hydroxy-4 : 6-dimethylbenzaldehyde has m. p. 48—49°. Its semicarbazone, a colourless powder, m. p. about 240°, according to the rate of heating; phenylhydrazone, colourless, lustrous needles, m. p. 126.5—127°; anil, yellow, silky needles, m. p. 88.5—89°; oxime, slender needles, m. p. 125—126°, and methyl ether, long, slender, colourless needles, m. p. 48—49°, are described. The oxidation of the aldehyde to the corresponding acid could not be effected, whereas its methyl ether is slowly transformed by potassium permanganate in the presence of sodium hydroxide into 2-methoxy-4 : 6-dimethylbenzoic acid, colourless, lustrous platelets, m. p. 167.5—168°. 2-Acetoxy-4 : 6-dimethylbenzonitrile, colourless needles, m. p. 49—50°, is prepared by the action of sodium acetate and acetic anhydride on the oxime of the hydroxyaldehyde; it is hydrolysed by alcoholic potassium hydroxide to 2-hydroxy-4 : 6-dimethylbenzonitrile, slender, colourless needles, m. p. 177—178°. 5-Benzeneazo-2-hydroxy-4 : 6-dimethylbenzaldehyde, matt, brown leaflets, m. p. 97.5—98° (m. p. 122° was observed on an isolated occasion), is prepared from the aldehyde and benzenediazonium chloride in alkaline solution; its sodium salt is sparingly soluble in water.

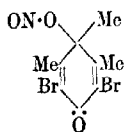
Hemellitenol [3 : 4 : 5-trimethylphenol], long, colourless needles, m. p. 107°, is prepared in 40% yield by the reduction of 4-hydroxy-2 : 6-dimethylbenzaldehyde by amalgamated zinc and hydrochloric acid according to Clemmensen's process. It is transformed by bromine into 2 : 6-dibromo-3 : 4 : 5-trimethylphenol, small leaflets, m. p. 142.5—143°, which is converted with difficulty by bromine at 100° into 2 : 6-dibromo-3 : 5-dimethyl-4-bromomethylphenol, m. p. 138.5—139.5°. The action of hot, concentrated nitric acid on the phenol bromide leads to the production of the ψ -quinol



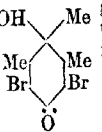
(I.)



(II.)



(III.)



(IV.)

(annexed formula, I), colourless, matted needles, m. p. 213°, which is converted by sodium hydroxide into the oxide (annexed formula, II), leaflets, m. p. indefinite, 156—160° (decomp.). Dibromohemellitenol is converted by cold, concentrated nitric acid into dibromohemellitylquinol (III), large monoclinic leaflets, m. p. 108°, which is transformed by boiling glacial acetic acid into dibromohemellityl- ψ -quinol (IV), long, slender, lustrous needles, m. p. 214—215°. Hemellitenol is remarkably stable towards cold concentrated nitric acid, by which it is converted at a higher temperature into dinitrohemellitylquinol, m. p. 146—147° (decomp.), which is trans-

formed by glacial acetic acid at 50° into *dinitrohemellityl- ψ -quinol*, slender, colourless needles, m. p. 213° . Hemellitenol is transformed by an aqueous solution of formaldehyde in the presence of slaked lime at 50° into *3:4:5-trimethyl-2:6-dihydroxymethylphenol*, small, colourless needles, m. p. 148° , which when the action is prolonged passes into a substance, m. p. above 360° , which has not been investigated closely; a similar change is observed in the presence of sodium hydroxide. A solution of the dihydroxy-alcohol in glacial acetic acid is converted by hydrogen bromide into *3:4:5-trimethyl-2:6-dibromomethylphenol*, short, colourless needles, m. p. $164-165^{\circ}$, which could not be reduced to pentamethylphenol by zinc and hydrochloric acid, the dihydroxy-alcohol being obtained. Hemellitenol couples with benzenediazonium chloride in the presence of sodium hydroxide solutions of varying concentrations to yield *6-benzeneazo-3:4:5-trimethylphenol*, slender, brownish-red needles, m. p. $126.5-127^{\circ}$.

3:5:6-Trimethylphenol, m. p. $93-94^{\circ}$, is prepared conveniently and in 40% yield by the reduction of *2-hydroxy-4:6-dimethylbenzaldehyde* with amalgamated zinc and hydrochloric acid. It is converted by concentrated nitric acid in the presence of glacial acetic acid into *2-nitro-3:5:6-trimethylphenol*, pale yellow leaflets, m. p. $78-79^{\circ}$. It couples with an equivalent amount of benzenediazonium chloride in the presence of sodium hydroxide to give a mixture of *4-benzeneazo-3:5:6-trimethylphenol*, lustrous, flattened, red needles, m. p. $154.5-156.5^{\circ}$, and *2:4-bisbenzeneazo-3:5:6-trimethylphenol*, small, brown crystals, m. p. $130.5-131.5^{\circ}$; increasing concentration of alkali hydroxide favours the production of the di-derivative.

H. W.

The Isomerism of the Oximes. X. Cinnam- and Nitrocinnam-aldoximes. OSCAR LISLE BRADY and CLIFFORD DANE THOMAS (T., 1922, **121**, 2098-2110).

The Interaction of Aldehydes or Ketones and Thiocarbamides in the Presence of Acids. II. JOHN TAYLOR (T., 1922, **121**, 2267-2272).

The Friedel-Crafts' Reaction. HEINRICH WIELAND and LUDWIG BETTAG (*Ber.*, 1922, **55**, [B], 2246-2255).—A further examination of the possibility that substitution in the benzene series is preceded by a primary additive process at a double bond, and that the mechanism of reaction is similar in the aromatic and aliphatic series (cf. Wieland and Sakellarios, A., 1920, i, 280; Wieland and Rahn, A., 1921, i, 782). The ability of substances to react with acetyl chloride and similar compounds in the presence of aluminium chloride has usually been ascribed to the presence in them of a mobile hydrogen atom, but indications of the production of a primary additive compound have been recorded by Darzens (A., 1910, i, 856) in the case of acetyl chloride and *cyclohexene*, and by Böeseken (A., 1913, i, 330) in that of tetrachloroethylene and chloroform. The isolation of the primary chloroketone from *cyclohexene* and acetyl chloride in the pure condition

is now described, and, further, it is shown that this substance is transformed into the unsaturated ketone under the normal conditions of the Friedel-Crafts' reaction. The difference in the behaviour of aliphatic and aromatic compounds during this synthesis is purely qualitative. The highly reactive aliphatic double bond allows addition to occur under conditions such that the primary additive compound is to some extent stable, whereas with the less reactive aromatic double bond addition is only possible in circumstances which cause the additive compound to be unstable. The catalytic function of aluminium chloride is attributed to its ability to weaken the bond between carbon and chlorine, and thus to facilitate the combination of the two addenda.

In the case of the synthesis of hydrocarbons according to Friedel and Crafts, it has not been found possible to adduce such definite experimental evidence. The cause lies in the slower velocity of the action of alkyl haloids, and the consequent predominance of the formation of resinous polymerides from the olefines under the influence of aluminium chloride; in addition, the newly-formed alkyl haloids have a marked tendency towards further reaction with the olefine. It has therefore not been possible to cause *n*-propyl chloride to react in the desired manner with ethylene, amylene, or cyclohexene, although it could be shown that products containing chlorine are produced, thus probably pointing to a primary additive change.

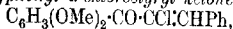
Aluminium chloride is added gradually to a solution of cyclohexene and acetyl chloride in carbon disulphide at -18° ; reaction takes place almost without evolution of hydrogen chloride and results in the formation of 2-chlorocyclohexyl methyl ketone and tetrahydroacetophenone, which cannot be separated from one another by fractional distillation. The unsaturated compound is decomposed by oxidising the mixture with potassium permanganate in the presence of acetone, and the chloro-ketone is isolated as a pale yellow, somewhat unstable liquid, b. p. $60-63^{\circ}$ (slight decomp.)/1 mm., through the semicarbazone, colourless leaflets, m. p. 163° (decomp.). It is transformed by further treatment with aluminium chloride in the presence of carbon disulphide into tetrahydroacetophenone. In a similar manner, cyclohexene and benzoyl chloride yield 2-chlorocyclohexyl phenyl ketone, a pale yellow, viscous liquid, b. p. $120-122^{\circ}$ (slight decomp.)/1 mm., which is further transformed by aluminium chloride and carbon disulphide into tetrahydrobenzophenone [semicarbazone, pale yellow prisms, m. p. 213° (decomp.)], in minimal yield (the direct preparation of tetrahydrobenzophenone from cyclohexene and benzoyl chloride also gives very poor yields). Acetyl chloride and β -methyl- β -butene give chloro-sec. isoamyl methyl ketone, $\text{CMe}_2\text{Cl}\cdot\text{CHMe}\cdot\text{COMe}$, a pale yellow, very unstable liquid with an odour resembling that of camphor.

H. W.

The Condensation of α -Halogeno-ketones with Aldehydes.
K. HUGO BAUER and FRITZ WERNER (*Ber.*, 1922, **55**, [B], 2494-2500).—It has been shown by Widman (*A.*, 1916, i, 406) that ω -bromo- or ω -chloro-acetophenone condenses with benzaldehyde

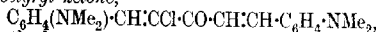
in the presence of sodium ethoxide with the formation of benzoyl-phenylethylene oxide. Condensation of these substances can also be brought about by hydrogen chloride or hydrogen bromide in the presence of glacial acetic acid; in all cases, $\alpha\beta$ -unsaturated α -halogeno-ketones appear to be the initial products, but the change may proceed further and result, by addition of hydrogen haloid, in the formation of $\alpha\beta$ -dihalogeno-ketones.

Phenyl styryl ketone dibromide, $\text{COPh}\cdot\text{CHBr}\cdot\text{CHBrPh}$, small, colourless crystals, m. p. $158-159^\circ$, is prepared by the action of hydrogen bromide on a solution of ω -bromoacetophenone and benzaldehyde in glacial acetic acid at the atmospheric temperature. Phenyl 3':4'-methylenedioxystryryl ketone dibromide, colourless leaflets, m. p. 152° , is obtained similarly from ω -bromoacetophenone and piperonal or by the addition of bromine to methylenedioxy-chalkone in carbon tetrachloride solution. 3:4-Dimethoxyphenyl styryl ketone dichloride, colourless crystals, m. p. $133-135^\circ$, is derived from ω -chloroacetoveratrone and benzaldehyde in the presence of hydrogen chloride, whereas the ketone and *p*-dimethylaminobenzaldehyde give 3:4-dimethoxyphenyl α -chloro-4'-dimethylaminostyryl ketone, intensely yellow leaflets, m. p. $129-130^\circ$. α -Bromoacetoveratrone, benzaldehyde, and hydrogen chloride form 3:4-dimethoxyphenyl α -chlorostyryl ketone,

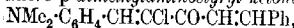


large, transparent cubes, m. p. $108-109^\circ$.

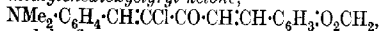
p-Dimethylaminobenzaldehyde condenses with chloroacetone in glacial acetic acid solution in the presence of hydrogen chloride to give a mixture of α -chloro-4'-dimethylaminostyryl methyl ketone, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CCl}\cdot\text{COMe}$, yellow leaflets, m. p. 115° (semicarbazone, a colourless, crystalline powder, m. p. $202-203^\circ$, phenylhydrazone, slender, pale yellow needles, m. p. $206-208^\circ$) and α -chloro-di-*p*-dimethylaminostyryl ketone,



m. p. 225° ; the latter may also be obtained by the action of sodium hydroxide on chloro-*p*-dimethylaminostyryl methyl ketone and *p*-dimethylaminobenzaldehyde dissolved in alcohol. Chloro-*p*-dimethylaminostyryl methyl ketone and benzaldehyde condense in aqueous alcoholic solution in the presence of sodium hydroxide to form styryl α -chloro-*p*-dimethylaminostyryl ketone,



dark, tile-red leaflets, m. p. $150-151^\circ$. α -Chloro- α -*p*-dimethylaminostyryl methylenedioxystryryl ketone,



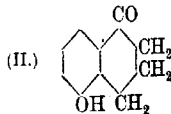
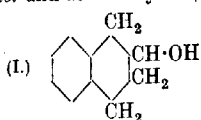
orange-coloured leaflets, m. p. 186.5° , is obtained similarly from chloro-*p*-dimethylaminostyryl methyl ketone and piperonal.

H. W.

Position of the Double Linking in Piperitone. II. A. R. PENFOLD (*Perf. Essent. Oil Rec.*, 1922, **13**, 322-323; cf. this vol., 259).—From the products of the action of neutral potassium permanganate on piperitone, in addition to diosphenol, the following acids were isolated: α -hydroxy- α -methyl- α -isopropyladipic

acid, m. p. 143.5°, γ -acetyl- α -isopropylbutyric acid, identified by means of its semicarbazone, m. p. 158°, and α -isopropylglutaric acid, m. p. 94—95°. The formation of these substances confirms the constitution of piperitone as Δ^1 -menthen-3-one, previously put forward. In view of the conflicting statements as to the m. p. of the oxime and semicarbazones of piperitone, these derivatives were again prepared; the oxime melts at 117—118° as stated by Simonsen (T., 1921, 119, 1644), the m. p. given by Read and Smith (T., 1921, 119, 779) being incorrect. Three semicarbazones were isolated, dl- α -semicarbazone, m. p. 225—226°, dl- β -semicarbazone, m. p. 175—176°, and the racemic semicarbazone, m. p. 188—189°. The best method for preparing piperitone hydroxylamino-oxime is to dissolve equal weights of the ketone, hydroxylamine hydrochloride, and potassium hydroxide in aqueous alcohol, and after keeping for some hours the whole solidifies to a crystalline mass of the oxime in almost quantitative yield. G. F. M.

Preparation of α -Keto-substituted Hydrogenated Naphthalenes. GEORG SCHROETER and TETRALIN G. M. B. H. (D.R.P. 352720; from *Chem. Zentr.*, 1922, iv, 158).— α -Naphthol and iso- or hetero-nuclear substituted α -naphthols, melted or in solution, are treated with hydrogen under pressure in amount corresponding with less than two molecules, in the presence of metallic catalysts. For example, colourless α -naphthol is mixed with tetrahydronaphthalene and a catalyst consisting of reduced nickel deposited on kieselguhr, and treated with hydrogen at 120—180° under a pressure of 10—20 atmospheres. After absorption of hydrogen corresponding with 1.5 molecules, the reaction is ended and the filtered liquid fractionated under reduced pressure. At 14 mm. pressure, the tetrahydronaphthalene distils over at 190°. α -Keto-tetrahydronaphthalene has b. p. 134—135°/14 mm. The distillate at higher temperatures is a mixture of α -naphthol and ar-tetrahydro- α -naphthol, which is again submitted to reduction. β -Naphthol similarly treated gives no ketone, but a little ar-tetrahydro- β -naphthol and ac-tetrahydro- β -naphthol (I).



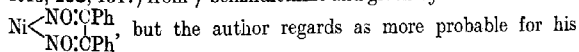
1:5-Dihydroxynaphthalene yields similarly, by reduction, 1-keto-5-hydroxytetrahydronaphthalene (II), colourless crystals, m. p. 156—157°. It forms a semicarbazone, m. p. 224°; an acetyl derivative; a methyl ether, and a phenylurethane. 1:8-Dihydroxynaphthalene gives, by reduction, 1-keto-8-hydroxytetrahydronaphthalene. 1-Hydroxy-5-acetylaminonaphthalene gives 1-keto-5-acetylaminotetrahydronaphthalene. G. W. R.

The Mechanism of the Formation of Benzoylbenzoin by Treatment of Benzoylmandelonitrile with an Alcoholic Solution of Sodium Ethoxide. HERBERT GREENE and ROBERT ROBINSON (T., 1922, 121, 2182—2196).

Dioximes. III. G. PONZIO (*Gazzetta*, 1922, **52**, ii, 145—160; cf. this vol., i, 627).—By the action of hydroxylamine on oximinobenzoylacetone, Ceresole (A., 1884, 1167) obtained a compound, m. p. 178°, which he regarded as one of the two possible α -dioximes of phenylmethyltriketone and is described in Beilstein's "Handbuch" (Vol. III, p. 270) as butyltrioneophendioxime, $\text{NOH}\cdot\text{CMe}\cdot\text{CBz}\cdot\text{NOH}$. The author finds, however, that the product of this reaction is a mixture of two benzoylmethylglyoximes which are not mere spacial isomerides. The action of nitrogen tetroxide on one of these oximes (termed the α -compound) yields α -oximino- β - ψ -nitrole- γ -ketophenylbutane, so that the two oximino-groups in this oxime are not equivalent to one another; with the second isomeride (β), however, nitrogen tetroxide gives a peroxide, furoxan, the two oximino-groups being hence equivalent, since each loses its hydrogen atom. From the chemical behaviour of the two compounds the conclusion is drawn that the α -form is an equilibrated mixture of the two tautomeric modifications, β -nitroso- α -oximino- γ -ketophenylbutane, $\text{NOH}\cdot\text{CMe}\cdot\text{CHBz}\cdot\text{NO}$, and $\alpha\beta$ -dioximino- γ -ketophenylbutane, $\text{NOH}\cdot\text{CMe}\cdot\text{CBz}\cdot\text{NOH}$, and that the β -form consists of the latter tautomeride alone. The β -form may be regarded as the stable form of the $\alpha\beta$ -dioxime of phenylmethyltriketone, since it results when the α -form is heated with various solvents or with a base. It is evident, therefore, that not all α -dioximes behave as if they contain the group $-\text{C}(\text{NOH})\cdot\text{C}(\text{NOH})-$, and that the isomerism of the different forms of an α -dioxime may depend on the possession of different structures by one of the two oximino-groups.

Since oximinobenzoylacetone contains an oximino-group in the same position as one of those in the α -isomeride of benzoylmethylglyoxime, it may be represented by the equilibrium $\text{NOH}\cdot\text{CAcBz} \rightleftharpoons \text{NO}\cdot\text{CHAcBz}$, the hydrogen atom of the oximino-group being mobile. On this basis, the formation, by the action of hydroxylamine, of two glyoximes, one an equilibrated mixture, is readily explainable.

Like all α -dioximes regarded by Tschugacev as *syn*-forms, $\alpha\beta$ -dioximino- γ -ketophenylbutane acts in aqueous solution on nickel, copper, cobalt, and iron (this vol., i, 17), forming with the first three metals complex salts derived from two molecules of the glyoxime by replacement of two atoms of hydrogen, one from each molecule, by an atom of the metal. The equilibrated mixture termed the α -modification does not attack these metals, but it yields a cupric salt derived from one molecule of the dioxime by replacement of two hydrogen atoms by an atom of copper. The only other known salt of this type is that obtained by Atack (T., 1913, **103**, 1317) from γ -benzildioxime and given by him the formula



but the author regards as more probable for his copper salt the structure $\text{O} \begin{array}{c} \text{N}=\text{CMe} \\ \diagup \quad \diagdown \\ \text{Cu}\cdot\text{CBz}\cdot\text{NO} \end{array}$.

The action of hydroxylamine on the α - and β -forms of benzoylmethylglyoxime yields two distinct phenylmethyltriketone trioximes; isomerism in the trioximes has not previously been

observed, and no explanation is now offered of the existence of these two modifications. Both the trioximes act, in aqueous solution, on nickel, forming two different complex salts, each derived from two molecules of trioxime by replacement of two oximinic hydrogen atoms by an atom of the bivalent metal. Neither of the two dioximes and neither of the two trioximes is obtainable directly from phenylmethyltriketone.

α-Benzoylmethylglyoxime, $\text{NOH}\cdot\text{CMe}\cdot\text{CBz}\cdot\text{NOH}$, crystallises in white, rectangular laminae, often united to pennate aggregates, m. p. 135° (decomp., turning green), and dissolves in alkali hydroxide or ammonia solution without coloration, and in cold, concentrated sulphuric acid, giving an orange-brown coloration turned deep brown by addition of phenol. In aqueous solution at 80 – 90° , it readily loses water, yielding benzoylmethylfuran, $\text{O} < \begin{smallmatrix} \text{N}\cdot\text{CMe} \\ \text{N}\cdot\text{CBz} \end{smallmatrix}$. Its copper salt, $\text{C}_{10}\text{H}_8\text{O}_3\text{N}_2\text{Cu}$, forms a somewhat

unstable, olive-green powder, and when heated slowly has m. p. about 195° (decomp.), whilst when heated rapidly it explodes at about 185° . The diacetyl compound, $\text{OAc}\cdot\text{N}\cdot\text{CMe}\cdot\text{CBz}\cdot\text{NOAc}$, crystallises in flattened, white prisms, m. p. 113° , and yields benzoylmethylfuran when heated with water.

α-Oximino-β-ψ-nitrole-γ-ketophenylbutane, $\text{NOH}\cdot\text{CMe}\cdot\text{CBz}\cdot\text{N}_2\text{O}$, forms white prisms, m. p. 111° (decomp.), and dissolves in concentrated sulphuric acid to a colourless solution which becomes emerald green when heated gently with phenol. Even dilute solutions of bases readily hydrolyse it, rupture of the carbon atom chain taking place between the ψ-nitrole and carbonyl groups; thus, with ammonia solution, it yields aminomethylglyoxime, $\text{NOH}\cdot\text{CMe}\cdot\text{C}(\text{NH}_2)\cdot\text{NOH}$, and benzamide.

β-Benzoylmethylglyoxime, $\text{C}_{10}\text{H}_{10}\text{O}_3\text{N}_2$, crystallises in white laminae or prisms, m. p. 193 – 194° (decomp.), and dissolves in alkali hydroxide or ammonia solution with a golden-yellow coloration and in concentrated sulphuric acid without coloration. The nickel salt, $(\text{C}_{10}\text{H}_9\text{O}_3\text{N}_2)_2\text{Ni}$, crystallises in flat, blood-red needles, m. p. 258° , decomposing at 260° , and is readily decomposed by mineral acids, but is stable towards acetic acid. The copper salt, $(\text{C}_{10}\text{H}_9\text{O}_3\text{N}_2)_2\text{Cu}$, forms a pale coffee-coloured, compact, microcrystalline powder, m. p. 201° (decomp.). The cobaltous salt is obtained as a brownish-violet, microcrystalline powder, which remains unmelted at 300° and readily forms colloidal solutions with various organic solvents and possibly also with alkali hydroxide solutions. The diacetyl derivative, $\text{OAc}\cdot\text{N}\cdot\text{CMe}\cdot\text{CBz}\cdot\text{NOAc}$, forms white prisms, m. p. 68° , and the dibenzoyl derivative, $\text{C}_{24}\text{H}_{18}\text{O}_6\text{N}_4$, white prisms, m. p. 220 – 221° (decomp.).

Benzoylmethylfuroxan, $\text{CH}_3\cdot\text{C}_2\text{N}_2\text{O}_2\cdot\text{COPh}$, crystallises in long, white needles, m. p. 70° , and is converted into the β-benzoylmethylglyoxime when reduced by means of zinc dust and acetic acid.

Phenylmethyltriketone-α-trioxime, $\text{NOH}\cdot\text{CMe}\cdot\text{C}(\text{NOH})\cdot\text{CPh}\cdot\text{NOH}$, forms white, prismatic needles, m. p. 204° (decomp.), and dissolves without coloration in alkali hydroxide or ammonia solution or

concentrated sulphuric acid. The *nickel* salt, $(C_{10}H_{10}O_3N_3)_2Ni$, an orange-yellow powder, decomposes unmelted at about 220° . The *triacetyl* derivative, $C_{16}H_{17}O_6N_3$, forms prisms, m. p. 111° .

Phenylmethyltriketone-β-trioxime forms white needles, m. p. 196° (decomp.), if heated rapidly, or a somewhat lower temperature if heated slowly. The *nickel* salt crystallises in lustrous, orange-red laminae, m. p. 236° (decomp.), or a lower temperature if heated slowly. The *triacetyl* compound forms large prisms, m. p. 107° .

The *cobaltous* salt of *dimethylglyoxime*, $(NOH:CMc:CMc:N:O)_2Co$, obtained by the action of aqueous dimethylglyoxime solution on strips of cobalt, forms a coffee-coloured powder with a violet lustre, and begins to undergo change, without melting, at about 200° .

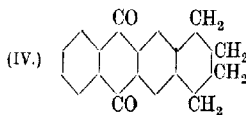
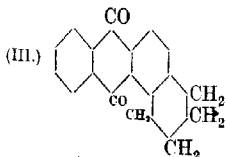
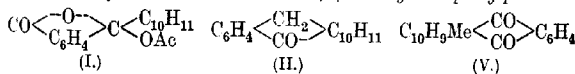
T. H. P.

The Labile Nature of the Halogen Atom in Organic Compounds. V. The Action of Hydrazine on the Halogen Derivatives of some Esters and substituted *cyclo*Hexanes. EDMUND LANGLEY HIRST and ALEXANDER KILLEN MACBETH (T., 1922, 121, 2169—2178).

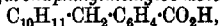
Preparation of Anthraquinone. CHARLES R. DOWNS (U.S. Pat. 1374721; from *Chem. Zentr.*, 1922, ii, 1055).—For the preparation of anthraquinone, anthracene in the state of vapour is passed, mixed with a gas containing oxygen, over vanadium oxide as catalyst, at about 375° . The temperature is maintained constant by introduction of mercury vapour into the reaction zone.

G. W. R.

Preparation of Hydrogenated Anthraquinones. TETRALIN G. M. B. H. (D.R.-P. 346673; from *Chem. Zentr.*, 1922, ii, 1079—1080).—Tetrahydronaphthalene or substituted tetrahydronaphthalenes are treated when gently heated with anhydrides of aromatic *o*-dicarboxylic acids, especially phthalic anhydride, in the presence of aluminium chloride and with addition of benzene and similar diluents. The γ -ketocarboxylic acids formed are changed into hydrogenated anthraquinones by condensing reagents, particularly fuming sulphuric acid. Tetrahydronaphthalene and phthalic anhydride give, at 60 – 70° in the presence of benzene and aluminium chloride, β -tetrahydronaphthoyl-*o*-benzoic acid; it forms crystals, m. p. 153 – 155° . It gives with acetic anhydride a crystalline *acetyl-lactone* (I), m. p. 135° . The *methyl* ester has m. p. 73 – 74° . By reduction of the acid, β -tetrahydronaphthylphthalide



(II)' and a α - β -tetrahydronaphthylmethylbenzoic acid,



are obtained. By the action of fuming sulphuric acid on tetrahydronaphthoyl- α -benzoic acid, a mixture of α -tetrahydronaphthylanthraquinone (III), m. p. 135°, and β -tetrahydronaphthylanthraquinone (IV), m. p. 211°, is obtained. The compounds are separated by fractional crystallisation. Both form yellow needles. They yield corresponding anthraquinols on reduction and readily give substituted derivatives with halogens, sulphuric acid, and nitric acid. 2-Methyltetrahydronaphthalene, obtained by the catalytic hydrogenation of 2-methylnaphthalene, is a colourless oil, b. p. 219–220°. It gives, on condensation with phthalic anhydride, 3-methyl-2-tetrahydronaphthoyl- α -benzoic acid, $\text{C}_{10}\text{H}_{10}\text{Me}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, needles, m. p. 160°. By the action of fuming sulphuric acid, 3-methyltetrahydro-2:1-naphthanthraquinone (V) is obtained; it forms yellow needles, m. p. 119°.

G. W. R.

Tetranitroanthrachryson. GUSTAV HELLER and PAUL LINDENER (*Ber.*, 1922, 55, [B], 2674–2679; cf. Heller and Skraup, A., 1913, i, 1207).—A more extended examination of the substance (cf. D.R.-P. 73605).

Tetranitroanthrachryson [2:4:6:8-tetranitro-1:3:5:7-tetrahydroxyanthraquinone] is prepared by the action of nitric acid (*d* 1.26) and concentrated sulphuric acid on a solution of anthrachryson in the latter acid; it crystallises in orange-coloured leaflets, which darken at 200° and explode at about 285°. It is remarkable that the entrance of the four nitro-groups occurs simultaneously so that unchanged original material remains if too little nitric acid is used. Its salts with the alkalis and ammonia are described. It is readily attacked by boiling aqueous ammonia, but the change appears to be so complicated that it is impossible to isolate a uniform material. Reduction does not occur smoothly, since the replacement of an amino-group by hydrogen occurs simultaneously with the complete conversion of the nitro- into the amino-group. The action of stannous chloride appears to lead to the formation of (?) triaminoanthrachryson, a black substance which is unchanged below 295°, whereas sodium hyposulphite gives the sodium salt of a triaminoanthrachryson, $\text{C}_{14}\text{H}_9\text{O}_2\text{N}_3\text{Na}_4$. Tetranitroanthrachryson reacts readily with aromatic bases in alkaline solution, giving dark dyes from which a homogeneous material could not be isolated.

The probability of the participation of the hydroxy-groups in the reactions just described has led to the preparation of 1:3:5:7-tetramethoxyanthraquinone, slender, yellow needles, m. p. 238°, by the action of methyl sulphate on anthrachryson in alkaline solution. The ether is transformed readily into 2:4:6:8-tetranitro-1:3:5:7-tetramethoxyanthraquinone, slender yellow needles, m. p. 258° (decomp.) after darkening at 220°, which is not affected by alcoholic potassium hydroxide solution. It is readily converted by aniline and aqueous sodium carbonate solution into 2:6-dinitro-4:8-dianilino-1:3:5:7-tetramethoxyanthraquinone, slender, dark

blue needles, which gradually decompose without melting above 300°.

H. W.

The Carbamides of Anthraquinone. M. BATTEGAY and J. BERNHARDT (*Chim. et Ind.*, 1922, 8, 305—306).—The three isomeric dianthraquinonylcarbamides, 1:1', 1:2', and 2:2' show a gradation in properties in which the 1:2'-isomeride approaches more nearly to the 2:2'- than to the 1:1'-isomeride. The 1:2' and the 2:2'-isomerides may be used as vat dyes by preliminary reduction in alkaline medium, but under similar conditions the 1:1'-isomeride very rapidly undergoes hydrolysis unless the temperature is kept below 18—20°, and then the carbamide is so little soluble as to render it useless as a dye. If, however, two hydroxy-, methoxy-, or benzoylamino-groups are substituted in it in positions para to the carbamide-group, then the products are no longer sensitive to destruction during reduction, and may be used as dyes.

W. G.

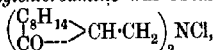
The Urethanes of Anthraquinone. M. BATTEGAY and J. BERNHARDT (*Chim. et Ind.*, 1922, 8, 307).—The group $\text{NH}\cdot\text{CO}_2\text{Et}$ exercises a greater auxochrome effect when introduced into the anthraquinone molecule than does the group $\text{NH}\cdot\text{COPh}$, both in the 1- and the 2-derivatives. The 1-urethanes, like the 1:1'-carbamides, are very sensitive to alkaline reduction, the product undergoing immediate hydrolysis. The introduction of a nitro-, a hydroxy-, a methoxy-, or a benzoylamino-group into the para-position in the urethanes does not check this hydrolysis as it did that of the carbamide (cf. previous abstract).

W. G.

Reduction Products of Hydroxymethylenecamphor. V. Coupling of Hydroxylamine with Methylenecamphor. H. RUPE and H. SCHMID (*Helv. Chim. Acta*, 1922, 5, 778—785).—Reaction between hydroxylamine and methylenecamphor in alcohol takes place between one molecule of the former and two molecules of the latter with formation of *di-camphomethylhydroxylamine* (C_8H_{14})₂ $\text{N}\cdot\text{OH}$, crystallising in colourless leaflets, m. p. 99.5—110.5°; its *hydrochloride* crystallises in fine, white leaflets decomposed by hot water; the neutral *oxalate* ($\text{C}_{20}\text{H}_{30}\text{O}_2\text{N}_2$)₂· $\text{C}_2\text{H}_2\text{O}_4$ forms white, microscopic leaflets, m. p. 169—169.5°. By stannous chloride and hydrochloric acid, the hydroxylamine derivative is reduced to di-camphomethylamine (cf. Rupe and Kussmaul, A., 1920, i, 622). Di-camphomethylhydroxylamine is readily oxidised by cupric acetate in alcoholic solution, but no definite products could be isolated. Better results were obtained with ferric chloride, and from the product was isolated a *compound*, $\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}$, white, microscopic crystals, sintering at 195°, m. p. 208—210°. Molecular-weight determinations by cryoscopic methods indicate a molecular weight from twice to four times that represented by the formula. Hydroxymethylenecamphor was expected to be present in the oxidation product, but was not found.

VOL. CXXII. i.

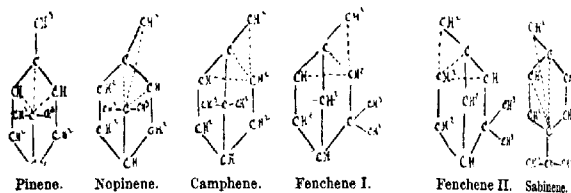
By the action of thionyl chloride on di-camphomethylhydroxylamine, *di-camphomethylchloroamine* was obtained,



a white, crystalline powder, becoming yellow at 135°, m. p. 202–205° (decomp.).

E. H. R.

The Formulæ of Dicyclic Terpenes. GEORGES DUPONT (*Bull. Soc. chim.*, 1922, [iv], 31, 897–909).—A theoretical discussion which the author maintains that the usually accepted formulæ for dicyclic terpenes are based mainly on the products obtained on oxidation with permanganate and do not accord with other reactions of the hydrocarbons. The suggestion is made that their properties are more consistently expressed by the introduction of free valencies or oscillating bonds into the formulæ: each terpene is dealt with from this point of view. On the above hypothesis, the formulæ—which are compared with the Baeyer benzene formula—should be written:



H. J. E.

Melting Point of Commercial Terpin. JOSÉ MARÍA CLAVERA (*Anal. Fis. Quím.*, 1922, 20, 243–246).—The melting point of freshly crystallised terpin hydrate, determined with rapid heating is 118.2°, which is higher than the previously accepted value. The anhydrous terpin has m. p. 104.7°. The melting point of terpin hydrate is considerably changed by small variations in the amount of water of crystallisation present. A curve is given showing the initial and final melting points of a series of mixtures varying from anhydrous terpin to terpin hydrate. The melting point is an untrustworthy criterion of purity. G. W. R.

The Preparation of Bornylene. HANS MEERWEIN and JACOB JOUSSEN (*Ber.*, 1922, 55, [B], 2529–2533).—The elimination of hydrogen chloride from bornyl chloride has previously led to the isolation of camphene instead of the expected bornylene. Since a high temperature (about 230°) is necessary for this process, its course can readily be explained in the light of the work of Meerwein and van Emster (this vol., ii, 751) according to which the loss of the acid is preceded by the transformation of bornyl chloride into *isobornyl* chloride and camphene hydrochloride. The successful preparation of bornylene depends therefore on the discovery of conditions under which this change does not occur or only takes

place very slowly. Preliminary work in this direction has been carried out with the more reactive isobornyl chloride, since the transformations occur in the same manner with either substance and the results obtained with isobornyl chloride are directly applicable to bornyl chloride.

The rate of decomposition (velocity of transformation) of isobornyl chloride by alkali alkoxides is found to diminish with increasing concentration of the alkali, with diminution of the water content of the mixture and with increase in the molecular weight of the alcohol employed. By applying these conditions to bornyl chloride, it is found possible to prepare nearly pure bornylene (solidifying temperature $108-107^{\circ}$ instead of 113° as recorded in the literature for the pure material) by the action of a 10% solution of potassium amyloxide in amyl alcohol at 230° . The high temperature necessary for the change is remarkable. Under similar conditions, bornyl bromide loses hydrogen bromide almost instantaneously at about 190° with the formation of an equally pure bornylene.

H. W.

The Constitution of the Terpene Present in the Essential Oil from *Andropogon Swarancusa*, Jones. JOHN LIONEL SIMONSEN (T., 1922, 121, 2292-2299).

The Composition of the Essential Oil of Turpentine. M. VÉZES and G. DUPONT (*Chim. et Ind.*, 1922, 8, 318-319).—Physical constants of the essential oil of Aleppo turpentine (from *Pinus halepensis*) are given, and it is shown that the composition of the fresh oil depends only on the variety of the conifer which has produced it.

W. G.

Essential Oils from *Myrica Gale*, L. M. SCHOOF (J. Pharm. Belg., 1921, 3, 769-773; from *Chem. Zentr.*, 1922, i, 1340-1341).—The following data were obtained for two essential oils obtained from *Myrica Gale*, L., by steam distillation. The first oil, separating directly from the distillate, has d_{25}^{15} 0.9068; $[z]_D^{25}$ $-8^{\circ} 46'$; n_D^{25} 1.4820; acid number, 1.5; saponification number, 17.8; ester number, 16.3; acetyl number, 39.2; combined alcohols ($C_{10}H_{18}O$), 4.4%; ester (linalyl acetate), 5.6%; free alcohols ($C_{10}H_{18}O$), 11.106%; iodine number, 168.84. The second oil, extracted from the aqueous distillate, has d_{25}^{15} 0.8956; $[z]_D^{25}$ $-5^{\circ} 9'$; n_D^{25} 1.4656; acid number, 1.8; saponification number, 18.19; ester number, 16.39; acetyl number, 36.4; combined alcohols ($C_{10}H_{18}O$), 4.5%; ester (linalyl acetate), 5.73%; free alcohols ($C_{10}H_{18}O$), 7.06%; iodine number, 56.70.

G. W. R.

Isoprene and Caoutchouc. V. The Hydrogenation of Caoutchouc and its Constitution. H. STAUDINGER and J. FRITSCHI (*Helv. Chim. Acta*, 1922, 5, 785-806).—The hydrogenation of caoutchouc and the decomposition products of the hydrogenation product were studied to get more evidence regarding the constitution of the substance. According to one theory, the caoutchouc molecule is composed of aggregations of comparatively

simple molecules, ring compounds formed from two or more isoprene molecules, held together by partial valencies. According to an opposing theory, the whole colloid molecule is formed by polymerisation of isoprene molecules in chains of such size that the unsaturated character of the molecule is lost. The experimental evidence cannot be reconciled with the first theory, but favours the second. The hydrogenation of caoutchouc was accomplished by heating it with hydrogen in presence of platinum at 270° and about 100 atm. Nickel did not promote complete hydrogenation under these conditions. The hydrogenated product has the composition $(C_5H_{10})_x$ and retains the completely colloidal character of caoutchouc. It is stable towards bromine, but in sunlight becomes slowly brominated, the brominated product still having the properties of caoutchouc. Were the first theory of the constitution of caoutchouc correct, hydrogenation would be expected to destroy the partial or residual valencies holding the large molecules together, giving products of simpler constitution. Hydro-caoutchouc can be regarded as a high molecular paraffin hydrocarbon with so large a molecule that, in effect, $C_nH_{2n+2} = C_5H_{20}$.

The distillation of caoutchouc and of the hydrogenated material in a high vacuum was studied. The decomposition of caoutchouc is less far-reaching in a vacuum than under normal pressure. At a pressure of 0.1 to 0.3 mm., distillation takes place between 275° and 320° . The products obtained were isoprene, about 3.1%, dipentene, about 8.8%, a hydrocarbon, $C_{15}H_{24}$, about 4.4%, and small quantities of hydrocarbons, $C_{20}H_{32}$ and $C_{25}H_{40}$. The compound $C_{15}H_{24}$ contains two double bonds, and is probably a hydro-naphthalene derivative, whilst $C_{20}H_{32}$ contains three double bonds and probably has a long aliphatic side chain. The depolymerisation of caoutchouc to form these products can be understood if the molecule contains a long chain of the form

$\cdot CH_2 \cdot CH_2 \cdot CMe \cdot CH \cdot CH_2 \cdot CH_2 \cdot CMe \cdot CH \cdot CH_2 \cdot CH_2 \cdot CMe \cdot CH \cdot CH_2 \cdot CH_2 \cdot$ etc., which may split into sections containing 4, 8, 12, etc., carbon atoms in a chain, the sections then forming closed ring systems. When hydrocaoutchouc is distilled, a higher decomposition temperature, $350-390^{\circ}$, is necessary. The decomposition products have the composition $(C_5H_{10})_x$ and in each case have only one double bond. The lowest product found was a pentene, b. p. $30-40^{\circ}$, which appeared to be β -methyl- Δ^4 -butylene since it gave methylethylketone on oxidation. From the higher boiling fractions were isolated, among others, a hydrocarbon, $C_{15}H_{20}$, and, as the highest boiling constituent, $C_{20}H_{30}$. The presence of such substances as the last in the decomposition products shows that hydrocaoutchouc itself must have an exceedingly high molecular weight. It cannot be vulcanised, and this fact supports the view that the vulcanisation of caoutchouc is a truly chemical process depending on the ethylene linkings and not an adsorption phenomenon. It is shown that in latex the caoutchouc is present in its normal molecular form and not in the form of simpler molecules which in the coagulation process combine to form caoutchouc.

E. H. R.

Betulin. HEINRICH SCHULZE and KURT PIEROH (*Ber.*, 1922, 55, [B], 2332–2346).—An extended investigation of betulin indicates that it is a member of a particular class of phytosterol-like dihydroxy-alcohols. The substance crystallises with one or one-half molecular proportion of ethyl alcohol which is very firmly retained and has been overlooked by previous workers. The empirical formula is $C_{32}H_{52}O_2$ or $C_{33}H_{54}O_2$. When heated with formic acid, it undergoes a remarkable transformation into *allobetulin* which appears to be closely related to β -amyrin and lupeol, whereas betulin shows great similarity to onocol isolated from *Ononios spinosa*.

Birch bark is extracted with aqueous ammonia and the dry residue is exhaustively treated with boiling alcohol. The bulk of the alcohol is removed and the residue is treated with an excess of lead acetate and evaporated to dryness. The dry mass is extracted with boiling benzene from which crude betulin separates. It is purified by crystallisation from alcohol from which it separates when the solutions are rapidly cooled in slender needles resembling asbestos (+2EtOH) or on slow cooling in coarse, lustrous, rhombic needles (+EtOH). It has m. p. 251–252°, $[\alpha]_D^{25} +19.96^\circ$ in pyridine solution. The diacetate crystallises in coarse, rhombic prisms, m. p. 216–217°, $[\alpha]_D^{25} +21.99^\circ$ in chloroform solution. Betulin is converted by phthalic anhydride into *betulin hydrogen phthalate*, slender, matted needles (from aqueous alcohol, +EtOH or +2H₂O), m. p. (not quite definite) 180–182° (decomp.), $[\alpha]_D^{25} +24.48^\circ$ when dissolved in chloroform; the corresponding *silver* salt is described.

Betulin is transformed by boiling formic acid (90–95%) into *allobetulin formate*, coarse, rhombic needles, m. p. 311–312°, $[\alpha]_D^{25} +51.08^\circ$ in chloroform solution, which is hydrolysed by alcoholic potassium hydroxide solution to *allobetulin*, monoclinic or triclinic platelets, m. p. 260–261°, $[\alpha]_D^{25} +48.25^\circ$ when dissolved in chloroform. Analysis of the substance and its derivatives are in agreement with the formula, $C_{32}H_{52}O_2$ or $C_{33}H_{54}O_2$, for *allobetulin* which appears to be isomeric with betulin. It contains only one hydroxyl group, the second oxygen atom being in ethereal linking. The conversion of betulin into *allobetulin* is not a specific action of formic acid, but appears to depend on the hydrogen-ion concentration; it can also be effected by acetic acid containing a little concentrated hydrochloric acid. In comparison with betulin, *allobetulin* and its derivatives are characterised by their higher melting point, smaller solubility, higher specific rotation, and greater stability towards chemical reagents. *allobetulin acetate* crystallises in hexagonal platelets belonging to the rhombic system; it has m. p. 277–278°, $[\alpha]_D^{25} +54.16^\circ$ in chloroform solution. *allobetulin* is converted by benzoic anhydride at 170° into *allobetulin benzoate*, apparently monoclinic platelets, m. p. 275–276°, $[\alpha]_D^{25} +70.26^\circ$, when dissolved in chloroform, by phthalic anhydride into *allobetulin hydrogen phthalate*, slender needles, m. p. 260–261° (slight gas evolution), $[\alpha]_D^{25} +58.20^\circ$ in chloroform (the *silver* salt is described), and by molten succinic anhydride into *allobetulin hydrogen succinate*, slender, lustrous leaflets, m. p. 265–266°, $[\alpha]_D^{25} +48.01^\circ$.

when dissolved in chloroform (the *silver* salt was analysed). *allo*. Betulin is oxidised by chromic acid in glacial acetic acid solution to *allobetulone*, colourless, rhombic needles, m. p. 230–231°, $[\alpha]_D^{25} +84.40^\circ$ in chloroform [*oxime*, leaflets, m. p. 285–290° (decomp.) when rapidly heated, *phenylhydrazone*, pale yellow leaflets, m. p. 223° (decomp.) after softening at 220°]. *allo*Betulin is converted by phosphorus pentachloride in the presence of chloroform into *apoallobetulin*, $C_{33}H_{50}O$ or $C_{33}H_{52}O$, lustrous, rhombic needles, m. p. 198–200°, $[\alpha]_D^{25} +74.78^\circ$ in chloroform solution. *Oxyallobetulin acetate*, $C_{32}H_{48}O_5Ac$ or $C_{32}H_{50}O_5Ac$, is prepared by the oxidation of *allobetulin acetate* dissolved in glacial acetic acid with chromic acid; it crystallises in leaflets which do not melt below 360°, $[\alpha]_D^{25} +54.34^\circ$ when dissolved in chloroform. It is hydrolysed by alcoholic potassium hydroxide solution to *oxyallobetulin*, slender, matted needles which sublime before melting.

H. W.

Tannins and Similar Compounds. X. The Tannin of the Native Oak. KARL FREUDENBERG and ERICH VOLBRECHT (*Ber.*, 1922, 55, [B], 2420–2423).—The tannin of the oak, isolated from the fresh leaves by means of the lead salt, is purified from free ellagic acid and admixed quercetin glucosides by extraction with ethyl acetate in a vacuum. It is accompanied by its own condensation products, from which it is freed by fractional precipitation from its alcoholic solution with ether. It is an amorphous, reddish-yellow material, freely soluble in water, alcohol, or acetone. It is strongly acidic. It has $[\alpha]_D$ about -35° . It contains 23–25% of combined ellagic acid, and about 5% of combined dextrose; the remainder of the molecule is an amorphous acid, termed *quercussic acid*. Warm, dilute mineral acids cause a more ready elimination of dextrose than of ellagic acid, the inactive hydrolytic product containing the residue of a compound of ellagic and quercussic acids. Continued hydrolysis effects the complete removal of ellagic acid. Dilute alkalis remove the whole of the ellagic acid in the cold, without, however, separating the dextrose. It appears, therefore, that oak tannin is a glucoside of quercussic acid, which is esterified to a depside with ellagic acid. Acid or alkaline hydrolysis of oak tannin results in the considerable destruction of quercussic acid. Tannase acts very slowly, but gives a uniform product which closely resembles the original material in physical properties, and is optically inactive and not hydrolysed by acid or alkali. Quercussic acid appears to be a bibasic acid of molecular weight about 800.

The degradation of oak tannin by tannase to quercussic acid is too tedious for preparative purposes. It is found, however, that, under definite conditions, *Aspergillus niger* grows on the solutions and thereby completes the degradation without decomposing the quercussic acid. Since, in addition, it is found that the galls of *Quercus pedunculata* contain the same tannin as the leaves, a convenient method of preparing quercussic acid is obtained. Treatment of it with molten potassium hydroxide has not led to the

isolation of definite products. Phloroglucinol is not formed; its isolation by earlier workers from oak tannin is probably attributable to the presence of quercetin.

H. W.

Constitution of Elsholtzic Acid. YASUHIKO ASAHINA and SATORU KUWADA (*J. Pharm. Soc. Japan*, 1922, No. 485, 565—579; cf. *ibid.*, 1918, No. 431).—For the complete determination of the constitution of elsholtzic acid, 2-methylfuran-3-carboxylic acid was prepared from dichloroethyl ether, acetoacetic ester, and ammonia by Benary's method (A., 1911, i, 319). It was converted into its chloride, brominated, hydrolysed by boiling with water and oxidised by means of silver oxide (Hill and Sawyer, A., 1894, i, 442), and the bromine atom contained in the nucleus removed by warming with ammonium chloride and zinc dust. The furan-2:3-dicarboxylic acid so obtained, colourless prisms, m. p. 221°, was proved to be identical with that obtained from elsholtzic acid. The constitution of elsholtzic acid and elsholtzic ketone are therefore, respectively,

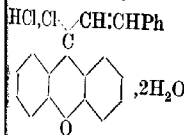
$$\begin{array}{c} \text{CH}\cdot\text{CMe} \\ | \\ \text{CH}-\text{O} \end{array} > \text{C}\cdot\text{CO}_2\text{H} \quad \text{and} \quad \begin{array}{c} \text{CH}\cdot\text{CMe} \\ | \\ \text{CH}-\text{O} \end{array} > \text{C}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHMe}_2$$

Methyl furan-2:3-dicarboxylate forms white crystals, m. p. 34°; the *monoanilide* crystallises in light yellowish-brown needles, m. p. 69—170°; the *dianilide* was not obtained. The product of the hydrolysis mentioned above was *bromo-2-hydroxymethylfuran-3-carboxylic acid*, fine, yellow needles, m. p. 116° (*monoacetate*, white needles, m. p. 94—95°). From the mother-liquor an *oxime* (impure) was obtained, which was converted into a nitrile, and then into furan-2:3-dicarboxylic acid.

K. K.

Poly-arylated Vinyl Carbinols and their Derivatives. II. Diarylstyryl Carbinols and the Products of their Transformations. KARL ZIEGLER and CURT OCHS (*Ber.*, 1922, 55, B], 2257—2277; cf. this vol., i, 151).—The recent publications of Meyer and Schuster (this vol., i, 540) and Skraup and Freundlich (this vol., i, 539) on halochromic phenomena with carbinols has caused the authors to give a further account of their work.

9-Styrylxanthy^l chloride hydrochloride (annexed formula) is obtained by treating a solution of 9-styrylxanthenol in benzene with concentrated hydrochloric acid. It forms small, coarse red crystals or golden leaflets which are stable in a closed vessel, but rapidly decompose on exposure to air. Its behaviour when heated varies greatly with the conditions of heating. The corresponding *bromide hydrochloride*, coarse red crystals, is prepared in an analogous manner. The chloride forms an extensive series of double salts with the chlorides of the heavy metals such as zinc chloride, mercuric chloride, ferric chloride, antimony trichloride, stannous chloride, and stannic chloride, of which the zinc compound, $\text{H}_{13}\text{OCl}\cdot\text{ZnCl}_2$, long, red needles, decomp. 188° after darkening



at 100°, and *ferric* compound, $C_{21}H_{15}OCl, FeCl_3$, carmine-red leaflets which gradually melts and decomposes at 160—180° after darkening at 145°, are described in detail. Analogous *salts* are formed from the bromide. The perhaloids, *chloride-perchloride*, *chloride-perbromide*, and *bromide-perbromide*, are characterised by the ease with which they lose the per-halogen, so that they could not be isolated in an analytically pure condition. 9-Styrylxanthenol, small, colourless crystals, m. p. 158—159°, is prepared by shaking an ethereal solution of the perchlorate or hydrochloride with sodium hydroxide or sodium carbonate; if traces of acid vapours and elevation of temperature are not scrupulously avoided during removal of the ether, *di-9-styrylxanthyli ether*, a colourless, microcrystalline powder, m. p. 172°, is obtained. 9-Styrylxanthyli chloride is converted by cold, absolute ethyl alcohol into 9-styrylxanthyli ethyl ether, small cubes or short prisms, m. p. 168—169° after previous darkening. The action of boiling glacial acetic acid on 9-styrylxanthenol, its ethers, or its chloride hydrochloride rapidly leads to the formation of a *substance*, colourless prisms, m. p. 241—242°; analyses of the product are in harmony with the formula, $O<\underset{C_6H_4}{\overset{C_6H_4}{C}}>C:C:CHPh$, but this simple constitution

is not in accord with determinations of the molecular weight and with the inability of the product to re-form the perchlorate when treated with perchloric acid; it is probably to be regarded as a polymerised allene derivative. 9-Styrylxanthyli perchlorate, on the other hand, is converted by boiling glacial acetic acid into a new stable *perchlorate*, dark brownish-red leaflets, decomp. 248°, which is transformed by boiling alcohol into the xanthene derivative, m. p. 241—242° (see above). Attempts to prepare 9-styrylxanthyli by the action of phenyl magnesium bromide on 9-styrylxanthyli perchlorate did not lead to the desired result. The reaction takes place energetically but without development of a trace of colour. The production of diphenyl cannot be established. The product appears to be 9-phenyl-9-styrylxanthenol, $O<\underset{C_6H_4}{\overset{C_6H_4}{C}}>CPh:CH:CHPh$,

colourless, microscopic prisms, m. p. 142—143°. (The analogous reaction between 9-phenylxanthyli perchlorate and magnesium phenyl bromide appears to yield 9-phenylxanthyli.)

Di-p-anisylstyryli carbinol, $(OMe\cdot C_6H_4)_2C(OH):CH:CHPh$, a voluminous, pale yellow powder which has not been caused to crystallise, is prepared in the same manner as 9-styrylxanthenol (the double *salts* of di-p-anisylstyrylmethyl chloride with ferric chloride and antimony trichloride have been prepared). The carbinol appears to be stable towards boiling ethyl alcohol containing a little acid; it is transformed by boiling glacial acetic acid into a *substance*, $(C_{23}H_{20}O_2)_2$, long needles, m. p. 188°, which is probably a polymerised allene derivative.

9-Styryldi-ββ'-naphthaxanthyli perchlorate (this vol., i, 153) has now been isolated as a stable, coffee-brown powder which darkens at 140°, slowly melts between 140 and 160°, and decomposes at 174°.

γ-Phenyl-αγ-di-p-anisylpropane-α-one,

$\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$,
 colourless crystals, m. p. 89–90°, is prepared by the action of magnesium *p*-anisyl bromide on *p*-anisyl styryl ketone. 2:4:4'-*Trimethoxybenzophenone*, colourless needles, m. p. 70–71°, is readily obtained from *p*-anisyl chloride and resorcinyldimethyl ether by Friedel and Crafts' reaction. 2:2'-*Dimethoxybenzhydrol*, colourless crystals, m. p. 85–86°, is prepared from salicylaldehyde methyl ether and magnesium *o*-anisyl bromide.

[With G. BREMER and F. THIEL.]—Halochromic salts, particularly perchlorates, can be obtained readily from tetra-arylallyl alcohols if the aryl groups are suitably chosen. Thus, *di-p-anisyl-(ββ-diphenylvinyl)methyl perchlorate*, m. p. 130–131°, is prepared in the same manner as *di-p-anisylstyrylmethyl perchlorate* from *ββ*-diphenylvinyl bromide and *di-p-anisyl ketone*. Free *diphenyl-di-p-anisylallyl alcohol* is an amorphous substance which appears to lose water with great readiness. The perchlorate is rapidly transformed by pyridine into pyridine perchlorate and *γγ-diphenyl-αα-di-p-anisylallene*, $\text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe})_2 \cdot \text{C} \cdot \text{CPh}_2$, colourless crystals, m. p. 102–103°, which is smoothly converted by perchloric acid into the original perchlorate.

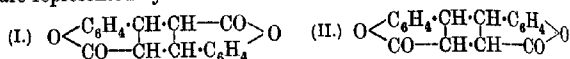
9-*ββ-Diphenylvinylxanthyl perchlorate*, $\text{O} \langle \text{C}_6\text{H}_4 \rangle \text{C} \langle \text{CH} \cdot \text{CPh}_2 \rangle \text{ClO}_4$, red needles, m. p. 166° (decomp.), is obtained smoothly by the action of *ββ*-diphenylvinyl bromide and magnesium on xanthone. It is readily hydrolysed to 9-*ββ-diphenylvinylidenexanthene*, $\text{O} \langle \text{C}_6\text{H}_4 \rangle \text{C} \cdot \text{C} \cdot \text{CPh}_2$, m. p. 205–206°, from which the original perchlorate is easily re-formed. The allene derivative becomes isomerised when subjected to the protracted action of boiling glacial acetic acid, giving a product, $\text{C}_{21}\text{H}_{18}\text{O}$, coarse, colourless cubes, m. p. 173–174°. *ββ-Diphenylvinylxanthyl chloride hydrochloride*, $\text{C}_{21}\text{H}_{20}\text{OCl}_2$, dark red, very unstable needles, is prepared by passing hydrogen chloride into a solution of 9-*ββ*-diphenylvinylidenexanthene in benzene to which a little acetyl chloride has been added. 9-*ββ*-Diphenylvinylxanthyl perchlorate reacts energetically with an ethereal solution of magnesium phenyl bromide, giving an intensely green solution from which colourless crystals of 9-*ββ-diphenylvinylxanthyl*, $\text{O} \langle \text{C}_6\text{H}_4 \rangle \text{C} \cdot \text{CH} \cdot \text{CPh}_2$, separate. The substance gives a pale yellow solution in cold benzene which becomes dark brown when heated, but returns to its original colour when again cooled. It is converted by air into the corresponding *peroxide*. The original green colour of the ethereal solution cannot at present be explained; it appears, however, to be due to a radicle, since it is discharged by contact with air.

H. W.

Biscoumaric Acids. A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, 25, 175–178).—In a recent communication (A., 1918, i, 303), the author has shown that the product

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of the action of light on coumarin is not identical with the hydrodicoumarin of Fittig and Dyson (T., 1887, **51**, 66). The author assumes that the product of illumination is formed from coumarin in the same way as α - and β -truxillic acids are formed from normal cinnamic acid by the production of a tetramethylene ring between the doubly linked carbon atoms of the two molecules. On this basis, four different biscoumarins may be formed, two of which are represented by each of the formulæ I and II.

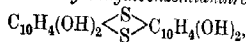


In addition to the biscoumarin of the author and hydrodicoumarin of Fittig and Dyson, a further biscoumarin has been isolated by Ström (A., 1904, i, 505), which, since it is formed from coumaric acid in the same way as α -truxillic acid from α -cinnamic acid, the author, in conformity with the names and structures assigned to the truxillic acids (A., 1918, i, 172), has termed α -biscoumarin, and the acid from which it is derived α -biscoumaric acid. This acid changes into α -biscoumarin at 250° and α -biscoumarin melts with decomposition at 318°. Methylation of α -biscoumaric acid with methyl sulphate gives the dimethyl ester of the dimethyl ether, which crystallises in needles, m. p. 133°, and is sparingly soluble in ether. The dimethyl ether, obtained by boiling the ester with alkali, melts at 261–262° and when heated with acetic anhydride at 210° yields the anhydride of the dimethyl ether of γ -biscoumaric acid, which crystallises in large, bright yellow crystals, m. p. 186–187°. The dimethyl ether melts at 234°. Heating α -biscoumaric acid with potassium hydroxide yields the acid corresponding with β -cocaic acid, m. p. 213°; this acid is named ζ -biscoumaric acid. The biscoumaric acid of the product of illumination of coumarin is termed λ -biscoumaric acid, and yields a dimethyl ester of the dimethyl ether which melts at 112–113°. Heating the dimethyl ether of λ -biscoumaric acid with acetic anhydride at 210° yields a non-crystallisable syrup, which on boiling with alkali yields the dimethyl ether of ϵ -biscoumaric acid, m. p. 203°. This transformation shows that the coumarin rings of the product of illumination are situated on different sides of the tetramethylene ring, and since the two coumarin rings are on different sides of the tetramethylene ring in α -biscoumarin, it follows that λ -biscoumarin has the structure II, and by removing a carboxyl group from one side of the tetramethylene ring to the other, an *o*-dihydroxy- ϵ -truxillic acid is formed. On melting λ -biscoumaric acid with potassium hydroxide, δ -biscoumaric acid is formed, m. p. 157°.

Dibenzothianthrenediquinone and Dinaphthathiophendiquinone. (Conversion of the Dithiin Ring into the Thiophen Ring.) KURT BRASS and LUDWIG KÖHLER (*Ber.*, 1922, **55**, [B], 2543–2568).—An account is given of the more extended examination of dibenzothianthrenediquinone, $C_{10}H_4O_2 \begin{smallmatrix} S \\ S \end{smallmatrix} C_{10}H_4O_2$ (cf.

Brass and Köhler, A., 1921, i, 435). The most remarkable property of the substance is the readiness with which it is converted into dinaphthathiophendiquinone, $S<\text{C}_{10}\text{H}_4\text{O}_2>\text{C}_{10}\text{H}_4\text{O}_2$, the dithiin being transformed into the thiophen ring.

The preparation of dibenzothianthrenediquinone is most conveniently effected by agitating an aqueous suspension of 2:3-dichloro- α -naphthaquinone (the method of obtaining the latter by chlorination of α -naphthaquinone in glacial acetic acid in the presence of iodine is described in detail) with the calculated quantity of sodium sulphide solution in the absence of air at the atmospheric temperature. Reaction occurs in accordance with the equation $8\text{C}_{10}\text{H}_4\text{O}_2\text{Cl}_2 + 12\text{Na}_2\text{S} + 3\text{H}_2\text{O} = 2\text{NaSH} + \text{Na}_2\text{S}_2\text{O}_3 + 16\text{NaCl} + 4\text{C}_{10}\text{H}_4\text{O}_2<\text{S}>\text{C}_{10}\text{H}_4(\text{OH})\cdot\text{ONa}$. The green monosodium salt of the quinhydrone is separated and treated with dilute nitric acid or chromic acid, whereby it is converted into the blue quinhydrone, which is oxidised further in the boiling solution to the quinone. Alternatively, an alkaline suspension of 2:3-dichloro- α -naphthaquinone is treated with hydrogen sulphide; in this case, reduction proceeds to the quinol stage, and the product is then oxidised as just described. The product has m. p. 302° (decomp.) after incipient decomposition at 280° , dinaphthathiophendiquinone being produced. A similar decomposition occurs slowly in the presence of boiling nitrobenzene. 1:14-Dihydroxydibenzothianthrenquinone, $\text{C}_{10}\text{H}_4\text{O}_2<\text{S}>\text{C}_{10}\text{H}_4(\text{OH})_2$, is obtained by the action of dilute acid on the green sodium salt described above. It crystallises in dark blue needles which are stable when dry, but readily oxidised to the quinone when moist. In consequence of atmospheric oxidation, it melts at 302° (m. p. of diquinone) when heated in an open capillary tube. Only one of its hydroxyl groups is capable of salt formation (the monosodium salt is described above). Both hydroxyl groups are readily acylated by acetyl or benzoyl chloride in the presence of pyridine, giving, respectively, 5:14-diacetoxydibenzothianthrenquinone, dark, olive-green crystals with a red reflex, m. p. (indefinite) $265-268^\circ$, and 5:14-dibenzoyloxydibenzothianthrenquinone, red rodlets or leaflets with a green reflex, m. p. (indefinite) 290° . 5:7:12:14-Tetrahydroxydibenzothianthren,



is obtained in colourless crystals by the action of carbon dioxide on a solution of its sodium salt in water; it is decidedly unstable and readily oxidised to the blue quinol. It forms a colourless methyl ether. Its acyl compounds are also colourless; 5:14-dihydroxy-7:12-diacetoxydibenzothianthren has m. p. about 262° after previous decomposition, whereas 5:7:12:14-tetra-acetoxydibenzothianthren crystallises in needles, m. p. (indefinite) $300-340^\circ$, and 5:7:12:14-tetrabenzoyloxydibenzothianthren forms rhombic plates, m. p. (indefinite) about 360° .

Dibenzothianthrenediquinone is quantitatively converted by a

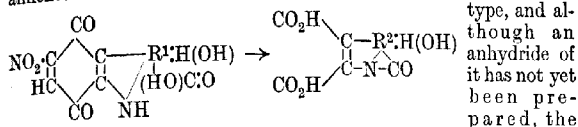
mixture of nitric acid (*d* 1.52) and water into *dibenzothianthrenediquinone sulphoxide*, $C_{10}H_4O_2 \begin{smallmatrix} S \\ \diagup \quad \diagdown \\ SO \end{smallmatrix} C_{10}H_4O_2$, yellow, hygroscopic needles. It is stable at the atmospheric temperature, but with rise in temperature exhibits a marked tendency to lose the sulphoxide sulphur atom and form the thiophen ring. It is reduced by hydrogen bromide to *dibenzothianthrenediquinone*, in which respect it differs from other sulfoxides. Hydrogen chloride acts similarly but more slowly. Zinc dust and glacial acetic acid or hydrogen iodide and glacial acetic acid convert it into the blue *quinhydrone*; since *dibenzothianthrenediquinone* is not formed during the process, it follows that the reduction of the keto-group precedes the loss of oxygen from the sulphonic group. *Dinaphthathiophendiquinone* is most conveniently prepared (with intermediate formation of the sulfoxide) by gradually heating *dibenzothianthrenediquinone* with fuming nitric acid (*d* 1.52). It crystallises in very stable, yellow needles, *m. p.* 278°; it sublimes at a higher temperature. It is reduced by stannous chloride in the presence of glacial acetic acid to 5:13-*dihydroxydinaphthathiophen-6:11-quinone*, $S \begin{smallmatrix} C_{10}H_4(OH)_2 \\ \diagup \quad \diagdown \\ C_{10}H_4O_2 \end{smallmatrix}$, dark green needles, *m. p.* (indefinite)

about 265°, which yields a *monoacetate*, blue rodlets or plates, *m. p.* (indefinite) about 290°, and a *diacetate*, pale red needles, *m. p.* (indefinite) 254°. 5:6:11:13-*Tetrahydroxydinaphthathiophen* is prepared by the reduction of *dinaphthathiophendiquinone* by hydrogen iodide in hot glacial acetic acid solution; it forms pale green needles which readily undergo oxidation; the corresponding *tetra-acetate* forms pale yellow plates, *m. p.* (indefinite) 271 (decomp.), whereas the *tetrabenzoate* crystallises in pale yellow, prismatic aggregates, *m. p.* about 330° (decomp.). H. W.

The Preparation of Histidine from Blood. S. DEMJANOVSKI (*Z. physiol. Chem.*, 1922, **122**, 93—97).—Details are given of a method by which a yield of 90 grams of crude histidine dihydrochloride may be obtained from 8½ litres of defibrinated blood. The hydrolysis is carried out in an autoclave with hydrochloric acid, at 1½ atmospheres pressure. W. O. K.

Strychnos Alkaloids. XXXIII. **The Degradation of Cacotheline by Bromine.** HERMANN LEUCHS, HANS MILDBRAND, and W. ROBERT LEUCHS (*Ber.*, 1922, **55**, [B], 2403—2415).—The degradation of cacotheline by bromine has been investigated previously by Hanssen (A., 1887, 505), who obtained a product which, on account of its behaviour towards sodium hydroxide, and of the formation of a mono-silver salt, he regarded as a mono-carboxylic acid. To this substance the empirical formula, $C_{19}H_{22}O_8N_2 \cdot 2H_2O$, is now assigned and the presence in it of two carboxyl groups is established, one of which is neutralised in the compound by the basic nitrogen atom. Four of the oxygen atoms are thus present in the carboxyl groups, whilst the fifth and sixth atoms are present in the acid amide and secondary alcoholic groups

of brucine, since the presence of aldehydic or ketonic groups could not be detected. One of the nitrogen atoms is present in the acid amide group, whilst the second is a basic, tertiary atom which enables the formation of quaternary ammonium salts and betaines. The probable course of the oxidative process is indicated by the annexed scheme. The new acid belongs thus to the maleic acid



presence of the double bond is established by the ready addition of two, but not more, atomic proportions of hydrogen. A remarkable point in the scheme outlined above is that the residue R^2 must contain two more atoms of hydrogen than R^1 , and that these can only be added as the result of an unusual reaction. In this connexion, it is recalled that cacotheline undergoes autoreduction in boiling aqueous solutions with production of a violet dihydro-derivative.

An aqueous solution of cacotheline, treated with hydrobromic acid and six atomic proportions of bromine, is heated on the water-bath and finally boiled until a clear solution is obtained, from which a yellow substance separates on cooling; this is purified by repeated treatment of its boiling aqueous solution with animal charcoal and precipitation with hydrobromic acid, whereby the hydrobromide, $\text{C}_{19}\text{H}_{22}\text{O}_6\text{N}_2\cdot\text{HBr}\cdot 2\text{H}_2\text{O}$, is obtained in colourless prisms or rectangular leaflets. The latter can be converted into the acid, $\text{C}_{19}\text{H}_{22}\text{O}_6\text{N}_2$, by boiling with lead oxide or silver carbonate in poor yield; decomposition is effected preferably with *N*-alkali hydroxide in boiling solution and evaporation of the solution until copious crystallisation has occurred in the boiling liquid. In this manner, the dihydrate is obtained as oblique prisms or four- or six-sided plates which dissolve in 26–27 parts of boiling water. Crystallisation from an ice-cold solution gives a *hexahydrate*, slender needles, which dissolve freely in warm water. The acid (as sodium salt) has $[\alpha]_D^{25} -37.0^\circ$ in aqueous solution. The *silver* salt, $\text{C}_{19}\text{H}_{21}\text{O}_6\text{N}_2\text{Ag}$, the *hydrochloride*, $\text{C}_{19}\text{H}_{22}\text{O}_6\text{N}_2\cdot\text{HCl}$, needles and prisms, the *hydrogen sulphate*, $\text{C}_{19}\text{H}_{22}\text{O}_6\text{N}_2\cdot\text{H}_2\text{SO}_4$, and the *nitrate*, $[\alpha]_D^{25} -30.0^\circ$ in aqueous solution, are described. The action of a methyl alcoholic solution of methyl iodide on the silver salt leads to the formation of the *methylbetaine* of the acid, $\text{C}_{20}\text{H}_{24}\text{O}_6\text{N}_2$, colourless prisms, $[\alpha]_D^{25} -5.6^\circ$ in aqueous solution, and a sparingly soluble product which is probably either an isomeric betaine or the acid, $\text{C}_{19}\text{H}_{22}\text{O}_6\text{N}_2$; it gives a sparingly soluble nitrate which has $[\alpha]_D^{25} -30.8^\circ$ in water, agreeing in this respect with the nitrate of the acid, from which, however, it differs in its water content. Treatment of the betaine with aqueous hydriodic acid gives the *methiodide* of the acid, $\text{C}_{20}\text{H}_{25}\text{O}_6\text{N}_2\cdot\text{I}\cdot 2\text{H}_2\text{O}$, pale yellow needles or prisms.

The *monomethyl ester hydrochloride*, $\text{C}_{20}\text{H}_{24}\text{O}_6\text{N}_2\cdot\text{HCl}$, slender,

colourless needles, is prepared by the action of methyl alcoholic hydrogen chloride on the acid at 20°. The corresponding free ester could not be caused to crystallise, whereas the *methiodide* forms pale yellow, oblique prisms. More drastic treatment of the acid with methyl-alcoholic hydrogen chloride gives the *dimethyl ester hydrochloride*, $C_{21}H_{26}O_6N_2.HCl$, coarse, rectangular prisms; the free ester crystallises in prisms, the *methiodide* in colourless, thick, hexagonal plates.

An aqueous solution of the hydrobromide of the acid, $C_{19}H_{22}O_4N_2$, is reduced by sodium amalgam; the resultant *acid*, however, cannot be caused to crystallise, and is isolated as its *methyl ester*, $C_{21}H_{26}O_6N_2$, colourless prisms, m. p. 143–147° (decomp.) after softening at 138°, m. p. about 132–135° in a vacuum. The preparation of the methyl ester *nitrate*, $C_{21}H_{26}O_6N_2.HNO_3$, coarse prisms, *hydrochloride*, rectangular prisms or leaflets, and *methiodide*, small prisms or long, rectangular plates, is described. The ester *hydrochloride* is hydrolysed by 12*N*-hydrochloric acid to the corresponding *acid hydrochloride*, $C_{19}H_{24}O_6N_2.HCl.3H_2O$, quadrate leaflets.

If the solution obtained by the oxidation of cacotheline with bromine is saturated with sulphur dioxide and preserved at 0°, crystals are deposited which evolve sulphur dioxide when boiled with water; these are converted by boiling 2*N*-hydrobromic acid solution into the *hydrobromide*, $C_{17}H_{26}O_3N_2.Br_2.HBr$, colourless, hexagonal plates. The corresponding *nitrate*, $C_{17}H_{26}O_3N_2.Br_2.HNO_3$, crystallises in rectangular leaflets or prisms. The free *base* is a granular powder which is decomposed by boiling water with re-formation of the hydrobromide. H. W.

Pyrroles and Hydroxypyrroles. HANS FISCHER and MARIE-ANNE HERRMANN (*Z. physiol. Chem.*, 1922, **122**, 1–25).—The following pyrrole compounds have been prepared as being related or analogous to certain derivatives of bilirubin.

Ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate, prepared from α -methyl- β -acetylsuccinic acid (*phenylhydrazone*, colourless crystals, m. p. 85°), forms a *diacetyl* derivative on boiling with acetic anhydride containing a trace of sulphuric acid, almost colourless needles, m. p. 220° (decomp.). Ethyl 2-hydroxy-3:5-dimethylpyrrole-4-carboxylate, which yields a colourless *monoacetyl* derivative, m. p. 118°, is reduced by hydrogen iodide and acetic acid, yielding practically all its nitrogen as ammonia, and so resembling bilirubin acid.

The nitro-derivative of ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate on reduction with zinc dust yields *ethyl 3-amino-2-hydroxy-5-methylpyrrole-4-carboxylate*, colourless prisms, m. p. 244°.

Ethyl 3-hydroxy-5-methylpyrrole-4-carboxylate condenses with benzaldehyde in presence of a small quantity of potassium hydrogen sulphate to yield *ethyl 3-hydroxy-2-benzylidene-5-methylpyrrole-4-carboxylate*, glistening, yellow needles, m. p. 228°; with *p*-dimethylaminobenzaldehyde to yield *ethyl 3-hydroxy-2-p-dimethylaminobenzylidene-*

5-methylpyrrole-4-carboxylate, ochre-yellow needles, m. p. 214° ; with acetic anhydride there is formed a *monoacetyl* derivative, colourless needles, m. p. 123° , and with benzoyl chloride in pyridine a tarry mass, from which has been isolated rhombohedral, colourless crystals, m. p. 127° . Similarly with diazobenzene chloride, a yellow dye is formed, $C_{14}H_{15}O_3N_3$, yellow scales, m. p. 240° ; with diazotised *p*-dichloroaniline, a similar compound, long, yellow needles, aggregated in bundles, m. p. 265° , is formed; and analogous compounds are obtained from *p*-nitroaniline and diazobenzene-sulphonic acid.

o-Nitrophenyl chloromercaptan condenses in benzene solution with ethyl 2:4-dimethylpyrrole-3-carboxylate to yield ethyl 5-*o*-nitrophenylthiol-2:4-dimethylpyrrole-3-carboxylate, yellow octahedra, m. p. $191-192^{\circ}$. Similarly, from ethyl 2:5-dimethylpyrrole-3-carboxylate is obtained ethyl 4-*o*-nitrophenylthiol-2:5-dimethylpyrrole-3-carboxylate, fine, yellow prisms, m. p. 189° ; from 3-acetyl-2:4-dimethylpyrrole, 5-*o*-nitrophenylthiol-3-acetyl-2:4-dimethylpyrrole, greenish-yellow crystals, m. p. 252° ; from 2:4-dimethyl-5-acetylpyrrole, 3-*o*-nitrophenylthiol-5-acetyl-2:4-dimethylpyrrole, a green compound, m. p. $217-218^{\circ}$; and from 2:3:5-trimethylpyrrole, 4-*o*-nitrophenylthiol-2:3:5-trimethylpyrrole. No definite compound could be isolated from the action of *o*-nitrophenyl chloromercaptan on bilirubin, the hæmatoporphyrin from urine or fæces, or mesohæmatoporphyrin, whilst it does not react with ethyl 1-phenyl-2:5-dimethylpyrrole-3-carboxylate or ethyl 3-acetyl-2:4-dimethylpyrrole-5-carboxylate.

Ethyl 2:4-dimethylpyrrole-3-carboxylate condenses in dry ether with sulphur monochloride to yield ethyl 5-disulphido-bis-2:4-dimethylpyrrole-3-carboxylate, fine, pale yellow prisms, m. p. 195° , and with sulphur dichloride to yield ethyl 5-sulphido-bis-2:4-dimethylpyrrole-3-carboxylate, almost colourless, long needles, m. p. 197° , and also the monosulphide. Similarly, from ethyl 2:5-dimethylpyrrole-3-carboxylate is obtained ethyl 4:4'-sulphido-bis-2:5-dimethylpyrrole-3-carboxylate, pale yellow leaflets, m. p. 272° , and impure ethyl 4:4'-sulphido-bis-2:5-dimethylpyrrole-3-carboxylate; whilst from 5-acetyl-2:4-dimethylpyrrole, only bis-5-acetyl-2:4-dimethylpyrrole-3'-disulphide, small prisms, m. p. 317° , could be obtained.

W. O. K.

Pyrroles. III. Ketones, Ketonic Acid Esters, and Ketonic Acid Nitriles of Substituted Pyrroles. HANS FISCHER, KARL SCHNELLER, and WERNER ZERWECK (*Ber.*, 1922, 55, [B], 2390-2403).—The Gattermann synthesis of aldehydes with hydrocyanic acid and the Hoesch synthesis of ketones have been applied to a series of substituted pyrroles. In many cases, reaction proceeds very smoothly. The nitriles used include acetonitrile, benzonitrile, mono-, di-, and tri-chloroacetonitriles, cyanogen, malonitrile, ethyl cyanoacetate, and ethyl cyanoformate. With dinitriles, only a onesided condensation is achieved. Chloroacetonitrile promises to be particularly useful on account of its

great reactivity and the readiness with which the halogen atom in the new compound is replaced by other groups. It appears likely to be useful in the examination of the products of the degradation of blood and bile pigments.

Ethyl 5-acetyl-2:4-dimethylpyrrole-3-carboxylate, m. p. 142°, is obtained by passing a slow current of dry hydrogen chloride into a mixture of ethyl 2:4-dimethylpyrrole-3-carboxylate and acetonitrile dissolved in anhydrous ether and subsequent decomposition of the *imine hydrochloride* primarily formed (orange-coloured crystals, m. p. 240°), with warm water. Ethyl 5-benzoyl-2:4-dimethylpyrrole-3-carboxylate, colourless needles, m. p. 108°, and the intermediate *imine hydrochloride*, lemon-yellow needles, m. p. 232°, are prepared similarly. Chloroacetonitrile and ethyl 2:4-dimethylpyrrole-3-carboxylate give an *imine hydrochloride*, m. p. 110°, and ethyl 5-chloroacetyl-2:4-dimethylpyrrole-3-carboxylate, $\text{NH} \begin{smallmatrix} \text{C}(\text{CO}\cdot\text{CH}_2\text{Cl})\cdot\text{CMe} \\ \text{CMe}=\text{C}\cdot\text{CO}_2\text{Et} \end{smallmatrix}$, colourless needles, m. p. 187°,

(*phenylhydrazone*, yellow needles, m. p. 164°). The chloro-compound is converted by a solution of dimethylamine in absolute alcohol into ethyl 5-dimethylaminoacetyl-2:4-dimethylpyrrole-3-carboxylate, colourless crystals, m. p. 95°. Ethyl 2:4-dimethylpyrrole-3-carboxylate condenses with ethyl cyanoacetate in the usual manner giving an *imine hydrochloride* and ethyl 3-carbethoxy-2:4-dimethylpyrrole-5-acetate, colourless needles, m. p. 145°. Cyanogen condenses with ethyl 2:4-dimethylpyrrole-3-carboxylate with the formation of 3-carbethoxy-2:4-dimethylpyrrole-5-glyoxylonitrile, $\text{NH} \begin{smallmatrix} \text{C}(\text{CO}\cdot\text{CN})\cdot\text{CMe} \\ \text{CMe}=\text{C}\cdot\text{CO}_2\text{Et} \end{smallmatrix}$, silvery leaflets, m. p. 165°, but does not

appear to react under similar conditions with 3-acetyl-2:4-dimethylpyrrole, or with ethyl 2:5-dimethylpyrrole-3-carboxylate; a crystalline substance could not be obtained from 2:4-dimethylpyrrole. Ethyl 5-cyanoacetyl-2:4-dimethylpyrrole-3-carboxylate, almost colourless needles, m. p. 234°, is prepared from ethyl 2:4-dimethylpyrrole-3-carboxylate and malononitrile or from ethyl 5-chloroacetyl-2:4-dimethylpyrrole-3-carboxylate and potassium cyanide.

Ethyl 2:5-dimethylpyrrole-3-carboxylate and chloroacetonitrile give an *imine hydrochloride*, coarse, pale yellow needles, which is converted by cold water into ethyl 4-chloroacetyl-2:5-dimethylpyrrole-3-carboxylate, colourless crystals, m. p. 130°. 2:4:5-Trimethylpyrrole is transformed in a similar manner into 3-chloroacetyl-2:4:5-trimethylpyrrole, colourless crystals, m. p. 193°, which is transformed by potassium cyanide into 3-cyanoacetyl-2:4:5-trimethylpyrrole, colourless crystals, m. p. 178°.

Ethyl cyanoformate transforms ethyl 2:4-dimethylpyrrole-3-carboxylate into ethyl 3-carbethoxy-2:4-dimethylpyrrole-5-glyoxylate, $\text{NH} \begin{smallmatrix} \text{C}(\text{CO}\cdot\text{CO}_2\text{Et})\cdot\text{CMe} \\ \text{CMe}=\text{C}\cdot\text{CO}_2\text{Et} \end{smallmatrix}$, dark yellow crystals, m. p. 82·5°, which is readily hydrolysed by aqueous sodium hydroxide to the corresponding acid, m. p. 192° (decomp.). When treated similarly,

ethyl 2:5-dimethylpyrrole-3-carboxylate gives an *imine hydrochloride*, and ethyl 3-carbethoxy-2:5-dimethylpyrrole-4-glyoxylate, $\text{NH} < \begin{array}{c} \text{CMe}=\text{C}\cdot\text{CO}\cdot\text{CO}_2\text{Et} \\ \text{CMe}=\text{C}\cdot\text{CO}_2\text{Et} \end{array}$, colourless needles, m. p. 102°; 3-

acetyl-2:4-dimethylpyrrole yields an *imine hydrochloride*, coarse needles, and ethyl 3-acetyl-2:4-dimethylpyrrole-5-glyoxylate, colourless crystals, m. p. 120°, which is readily hydrolysed to the corresponding *acid*, pale yellow crystals, m. p. 178° (decomp.).

[With MAX SCHUBERT.]—A mixture of crude hæmopyrrole and chloroacetonitrile dissolved in ether is converted by dry hydrogen chloride into an imine hydrochloride which is transformed by hot water into a *chloroacetyl* derivative, $\text{C}_{10}\text{H}_{14}\text{ONCl}$, pale pink needles, m. p. 127°; the latter is converted by hydriodic and glacial acetic acids into hæmopyrrole [2:3-dimethyl-4-ethylpyrrole] identified as the picrate, m. p. 121°. H. W.

"Graphites" from Pyrrole and from Thiophen. R. CIUSA (*Gazzetta*, 1922, 52, ii, 130—131).—Following Ciamician and Ciusa's supposition (A., 1921, i, 329) that the existence of saturated complexes, C_6 , C_4HN , and C_4S , is possible, the author pointed out (*Atti R. Accad. Lincei*, 1921, [v], 30, i, 468) that such complexes should exhibit a marked tendency to polymerise to graphite from benzene and to the compounds $(\text{C}_4\text{HN})_n$ and $(\text{C}_4\text{S})_n$, which might be termed graphites from pyrrole and thiophen, respectively. It is now found that tetra-iodopyrrole yields at 150—200° the compound $(\text{C}_4\text{HNI})_{2n}$, and at an incipient red heat the compound $(\text{C}_4\text{HN})_n$, which forms black, graphitic scales and may be regarded as graphite from pyrrole. Similarly, when heated to incipient redness in a current of inert gas, tetra-iodothiophen gives the graphitic compound $(\text{C}_4\text{S})_n$. An analogous compound was obtained by Pauly (A., 1913, i, 1311) from tetra-iodoglyoxaline. With each of these tetra-iodo-derivatives, three iodine atoms are expelled simultaneously at a comparatively low temperature, whilst the fourth atom is eliminated in a succeeding phase at a higher temperature. Further, *tetra-iodofuran*, m. p. 145°, begins to lose iodine at 160° and decomposes at 262°, leaving a black residue similar to the other "graphites." T. H. P.

The 4-Piperidone Ring. L. RYZICKA and C. F. SEIDEL (*Helv. Chim. Acta*, 1922, 5, 715—720).—If the polymerisation of 4-piperidone is due to reaction between the keto- and the imino-groups, replacement of the hydrogen of the latter group by another radicle should prevent it. Such a substituted piperidone was prepared as follows. Ethyl $\beta\beta'\beta''$ -nitrilotripropionate (A., 1921, i, 53), $\text{N}(\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_3$, was condensed in benzene solution with sodium ethoxide and from the product was prepared ethyl 4-*keto-piperidinepropionate*, a viscous, colourless oil, b. p. 100—110°/0.5 mm. This ester can be distilled unchanged in a vacuum and does not polymerise. By reduction with hydrogen and platinum black in acetic acid solution, it gave ethyl 4-hydroxypiperidinepropionate, b. p. 125°/0.5 mm., benzoate, m. p. 195°.

An attempt was made to prepare the compound in the pyrrolidine

series analogous to 4-piperidone. By condensing ethyl β -iodopropionate with ethyl glycine, the *ethyl iminoacetatepropionate*, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, was obtained, b. p. $100-105^\circ/0.1$ mm. This was condensed by means of sodium, as in the preparation of 4-piperidone (*loc. cit.*), but, although the reaction appeared to proceed normally, pure products could not be isolated. Similarly, the condensation of the *benzoyl* derivative (b. p. $170-180^\circ/0.3$ mm.) gave no result. On the other hand, condensation of ethyl benzoyl- $\beta\beta'$ -iminodipropionate with sodium went normally and from the product was prepared the previously described dibenzylidene-4-piperidone (*loc. cit.*).

E. H. R.

Preparation of Dialkylamides of Nicotinic Acid. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 184625).—Dialkylamides of nicotinic acid are prepared by the interaction of a haloid or ester of the acid and a dialkylamine (cf. this vol., i, 866). Thus *nicotinodipropylamide* is obtained by heating nicotinyl chloride with dipropylamine hydrochloride at 180° . It is a yellow oil, b. p. $184^\circ/17$ mm. Similarly, the *piperidide* of nicotinic acid is obtained as a viscid oil, b. p. 310° , by heating the acid bromide with piperidine hydrobromide.

G. F. M.

New Isomerism in the Isatin Series. V. GUSTAV HELLER (*Ber.*, 1922, 55, [B], 2681—2697).—Previous investigations in the isatin series have shown that, in addition to the lactam form, $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{NH}$, which is common to isatin and its substitution

products, the lactim form, $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{N}\text{OH}$, has an independent existence in the case of 5:7-dimethylisatin, and that the third (isatole) form, $\text{C}_6\text{H}_4\langle\text{C(OH)}\rangle\text{N}$, is obtainable in several instances.

The problems of the series are further complicated by the formation of a fourth form of unknown constitution which is characterised by its high melting point and insolubility in alkali and of bimolecular isatins (isatoids) which are at present known only as their *O*-alkyl ethers. The present communication is mainly devoted to a description of dihalogenated isatins.

The course of the action of benzoyl chloride on isatin silver salts, in so far as isomerides of the isatins are concerned, is characterised by the primary production of the lactim form which only remains in a stable condition in the case of 5:7-dimethylisatin; with isatin, 5-chloro-, 5-bromo-, 5:7-dichloro-, and 4:5:7-trimethyl-isatin, the action proceeds further to the isatole, and with 5:7-dibromoisatin, 4-chloro-5-bromoisatin, and to a less extent with 5:7-dichloroisatin, to its final stage, thereby producing the form which is insoluble in alkali. Dimethylisatin lactim can be converted by alkali into the isatole, which, like dichloro- and trimethyl-isatole, is transformed into the fourth variety by recrystallisation from glacial acetic acid. This treatment does not have the same effect with the simplest isatole, and, in this case, the "insoluble" isomeride is yet unknown.

[With WALTER BENADE and OTTO HOCHMUTH.]—5 : 7-Dibromoisatin is readily converted by warm sodium carbonate solution into sodium dibromoisatoate; the corresponding acid, m. p. 248—249°, gives a somewhat sparingly soluble bisulphite compound. 5 : 7-Dibromoisatin silver, a greyish-violet substance, prepared by the action of a hot aqueous silver acetate solution on 5 : 7-dibromoisatin dissolved in hot alcohol, is transformed by benzoyl chloride in the presence of benzene mainly into 5 : 7-dibromo-N-benzoylisatoic acid, aggregates of needles, m. p. 207—208° (decomp.); in addition, a small quantity of the fourth dibromoisatin, slender needles, m. p. above 300°, is obtained. 5 : 7-Dibromo-N-benzoylisatin is prepared by the action of acetic anhydride on dibromobenzoylisatoic acid; it forms coarse, yellow crystals, m. p. 161—162°. 5 : 7-Dibromo-N-acetylisatin, yellow plates, m. p. 133°, is prepared by the action of acetyl chloride on the corresponding silver salt in the presence of benzene; it is converted by dilute sodium hydroxide solution into 5 : 7-dibromo-N-acetylisatoic acid, colourless needles, m. p. 204°. 5 : 7-Dibromoisatin silver is transformed by methyl iodide in the presence of benzene into the corresponding lactim ether, red crystals, m. p. 164—165°, which could not be converted smoothly into an isatoid. It is transformed by phenylhydrazine in the presence of light petroleum into 5 : 7-dibromoisatin- α -phenylhydrazone, dark red needles, m. p. 218° (decomp.), and by aniline into a mixture of 5 : 7-dibromoisatin- α -anilide, short brown rods, m. p. 189°, and 5 : 7-dibromoisatinanil, pale blue needles, m. p. 174—175°; the di-anil, $C_{30}H_{13}N_8Br_2$, dark red needles, m. p. 236—237°, is prepared by the further action of aniline on the anilide. 5 : 7-Dibromoisatin-dianil silver, a blue precipitate, is prepared by the action of silver acetate on an alcoholic solution of the di-anil. The salt is particularly remarkable because it does not contain oxygen, and its formation is precisely analogous to salt formation with oxygenated isatins. The sodium and potassium salts of 5 : 7-dibromoisatin are described; the compounds are much more stable than the corresponding isatin derivatives.

4-Chloro-5-bromoisatin silver, a bluish-grey salt, is mainly converted by benzoyl chloride in the presence of benzene into 4-chloro-5-bromo-N-benzoylisatin, coarse, yellow crystals, m. p. 196°, which is converted by warm dilute alkali into 4-chloro-5-bromo-N-benzoylisatoic acid, m. p. 186°. A dark-coloured, non-crystalline substance which does not dissolve in alkali is also produced in small amount; it probably belongs to the fourth series of isatin isomerides. Treatment of the silver salt with methyl iodide in the presence of benzene causes the slow formation of the corresponding O-methyl ether, m. p. (indefinite) 173°, which could not be obtained in the pure condition. It is converted by phenylhydrazine into 4-chloro-5-bromoisatin-2-phenylhydrazone, slender, dark red needles, m. p. 235° (decomp.), and by aniline into the corresponding anilide, m. p. 276—277° (decomp.).

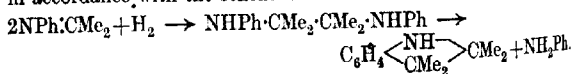
5 : 7-Dichloroisatin silver is converted by acetyl chloride in the presence of benzene into 5 : 7-dichloro-N-acetylisatoic acid, prisms, m. p. 204° (decomp.), which is transformed by acetic

anhydride into 5:7-dichloroisatin. The silver salt is converted by benzoyl chloride mainly into 5:7-dichloro-N-benzoylisatoic acid, $\text{NHBz} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$, colourless needles, m. p. 215° (decomp.). In addition to the primary product of the change, 5:7-dichloro-N-benzoylisatin, $\text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO} \cdot \text{NBz}$, yellow plates, m. p. 146° , is formed in very small quantity; it is obtained readily by the action of acetic anhydride on 5:7-dichloro-N-benzoylisatoic acid. 5:7-Dichloroisatole, m. p. 205° (slight decomp.), is also produced; its properties are similar to those of the simplest isatole in that it does not give the indophenin reaction, does not combine with phenylhydrazine, and dissolves in dilute sodium hydroxide solution to a carmine red solution which yields dichloroisatin on addition of mineral acids. 5:7-Dichloroisatole is unstable in solutions in organic media and is transformed by recrystallisation from glacial acetic acid into 5:7-dichloroisatin IV, red crystals, m. p. 313° . 5:7-Dichloroisatin methyl ether, red prisms, m. p. 158° , is prepared in the usual manner from the silver salt and methyl iodide (this reaction does not appear to be influenced by the presence of substituents); it is very stable towards light. The corresponding α -phenylhydrazone crystallises in dark red needles, m. p. $217\text{--}218^\circ$ (decomp.). The lactim ether is converted with relative ease by acetic anhydride into tetrachloromethylisatoid, m. p. 127° , followed by re-solidification at about 180° and re-melting at about 222° , which is transformed by hydrogen bromide and glacial acetic acid into dichloroisatin.

Re-examination of the action of benzoyl chloride on 5:7-dimethylisatin silver has shown that N-benzoyl-5:7-dimethylisatoic acid, colourless tetrahedra, m. p. 208° (decomp.), is produced during the action. 5:7-Dimethylisatin O-methyl ether, dark red prisms, m. p. $140\text{--}141^\circ$ [α -phenylhydrazone, red rodlets, m. p. 234° (decomp.)] is very stable towards light; it is converted by acetic anhydride or boiling toluene into 5:7-dimethylisatoid, red, crystalline plates, m. p. 237° (previously described as dimethylisatin-II methyl ether).

7-Methylisatin dissolved in alcohol does not give a normal silver salt with silver acetate; the product when heated with acetyl chloride or benzoyl chloride in the presence of benzene regenerates methylisatin. In other respects, the compound exhibits little activity, the only readily preparable derivative being N-acetyl-7-methylisatin, yellow platelets, m. p. 163° , which is converted by alkali into N-acetyl-7-methylisatoic acid, m. p. 175° . H. W.

Keto-anils. IV. Reduction Products of Keto-anils. E. KNOEVENAGEL (*Ber.*, 1922, 55, [B], 2300—2321; cf. this vol., i, 750, 751).—The reduction of acetoneanil with sodium and alcohol leads to the formation of 2:2:3:3-tetramethylindoline, in accordance with the scheme:



Acetone-*p*-tolil and acetone- α -naphthil behave similarly; the latter

case is of particular interest, since the intermediate compound can be isolated.

Acetoneanil is reduced by sodium and boiling ethyl alcohol to 2:2:3:3-tetramethylindoline, a colourless, crystalline substance, m. p. 39.5°. The base dissolves readily in cold dilute acetic acid, but does not yield a carbonate. It is stable towards hydrogen chloride at 240–280°, and towards mercuric acetate at 150°. It readily reduces alkaline potassium permanganate solution. It gives a hydrochloride, m. p. 201–207° (decomp.), a picrate, m. p. 74°, and an acetyl derivative, m. p. 83°. It is converted by molecular quantities of sodium nitrite and hydrochloric acid into the nitroso-derivative, m. p. 44.5°, which is readily isomerised by hydrochloric acid to 5-nitroso-2:2:3:3-tetramethylindoline hydrochloride, unstable, green crystals, m. p. (indefinite) 170° (decomp.). Attempts to reduce acetoneanil electrolytically at a lead cathode were unsuccessful.

Acetone-*p*-tolil is reduced by sodium and ethyl alcohol or, less advantageously, by zinc and hydrochloric acid (20%) to *p*-toluidine and 2:2:3:3:5-pentamethylindoline, a yellow liquid which does not solidify after prolonged preservation in a freezing mixture. The hydrochloride, m. p. 201–205° (decomp.), acetyl derivative, a pale yellow substance, m. p. 51°, b. p. 165–167°/14–15 mm., nitroso-compound, pale brown crystals, m. p. 48.5°, picrate, a reddish-brown salt, m. p. 144°, and oxalate are described.

Acetone- α -naphthil, a viscous, yellow liquid, b. p. 200–203°/12 mm., which could not be caused to crystallise, is prepared by heating a mixture of acetone and α -naphthylamine with a little iodine. It is hydrolysed by boiling hydrochloric acid (20%). The corresponding hydrogen oxalate, m. p. 167.5°, and picrate, slender, pale yellow needles, m. p. 210°, are described. It is reduced by sodium and ethyl alcohol at a temperature not exceeding 105° to acetone-ar-tetrahydro- α -naphthil, a greenish-yellow liquid which darkens gradually on exposure to air, b. p. 193–196°/14–15 mm. It does not form a carbonate. The corresponding hydrochloride forms coarse crystals, m. p. 199° (acetone- α -naphthil hydrochloride crystallises in slender, matted needles, m. p. 215°, after darkening and incipient decomposition at 180°); the hydrogen oxalate, colourless needles, m. p. 152–153°, and the picrate, yellowish-brown crystals, m. p. 175–185° (decomp.), are described. The tetrahydro-naphthil is hydrolysed by boiling hydrochloric acid (20%) to acetone and ar-tetrahydro- α -naphthylamine. Reduction of acetone- α -naphthil at a higher temperature (see above), either with sodium and ethyl alcohol under increased pressure or with sodium and amyl alcohol, leads to the formation of 2:2:3:3-tetramethyl-ar-tetrahydro- α -naphthindoline, a pale yellow liquid which is stable towards light; the colourless hydrogen oxalate, m. p. 183°, and the picrate, m. p. (indefinite) 163° after darkening at 150°, are described.

H. W.

The Quaternary Salts of Quinaldic Acid. WILLIAM HOBSON
MILLS and FRANCES MARY HAMER (T., 1922, 121, 2008–2014).

Doebner's Reaction. IV. R. CIUSA (*Gazzetta*, 1922, 52, ii, 43—48; cf. A., 1915, i, 894, 895; 1921, i, 195).—2-Phenyltetrahydro- β -naphthacinchonic acid, now obtained in larger quantity, crystallises in white scales, m. p. 226°, and, like its methyl ester, m. p. 134°, and its salts, gives solutions exhibiting slight blue fluorescence; the alkali metal salts are oily and the silver and lead salts of abnormal constitution. On prolonged boiling with alcohol, the acid yields phenyl- β -naphthaquinoline, m. p. 188°, together with other compounds not identified. This reaction is similar to that observed by Simon and Mauguin (A., 1907, i, 725; 1908, i, 296), who found that when dihydro-2-phenyl- β -naphthaquinoline-3:4-dicarboxylic acid is heated in alkaline solution, 2-phenyl- β -naphthacinchonic acid and 2-phenyl- β -naphthaquinoline are formed; as already shown, the dihydro-acid loses a carboxyl group from the β -position and then oxidises itself to 2-phenyl- β -naphthacinchonic acid, with simultaneous formation of the tetrahydrogenated acid, which is transformed into the corresponding non-hydrogenated base on boiling.

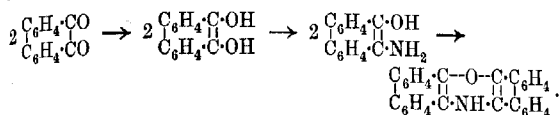
The action of benzylidene- α -naphthylamine on ethyl oxalacetate (cf. Simon and Mauguin, *loc. cit.*) yields: (1) 2-Phenyl- β -naphthaquinoline-3:4-dicarboxylic acid, m. p. 152°; Simon and Mauguin gave m. p. 162°. (2) A dimeride of benzylidene- β -naphthylamine which crystallises in colourless needles, m. p. 200°, yields benzaldehyde (2 mols.) and β -naphthylamine (2 mols.) when hydrolysed by means of dilute sulphuric acid, and may be represented provisionally by the annexed formula.

(3) Ethyl 2-phenyl- β -naphthaquinoline-3:4-dicarboxylate, already described by Simon and Mauguin (*loc. cit.*).
 α -Pyrrolicinchonic acid, $C_{14}H_{10}O_2N_2$, prepared by condensation of 2-acetylpyrrole with isatin in presence of potassium hydroxide, crystallises in small, yellow needles, and blackens without melting at 310°; its sodium salt ($+2\frac{1}{2}H_2O$) was analysed.

α -Furylcinchonic acid, $C_{14}H_8O_3N$, similarly prepared from 2-acetyl-furan and isatin, forms yellow needles, m. p. 149°. T. H. P.

Preparation and Mechanism of Formation of Phenanthroxazine. B. FORESTI (*Gazzetta*, 1922, 52, ii, 90—96; cf. this vol., ii, 524).—In the preparation of 9-amino-10-hydroxyphenanthrene by the reduction of phenanthraquinone monoxime in alcoholic solution by means of hydrogen sulphide, sulphur and impure phenanthroxazine are precipitated, the aminohydroxyphenanthrene undergoing condensation at the boiling point of the alcohol. This condensation takes place more rapidly and yields a purer product if a suspension of the hydrochloride of the base in nitrobenzene or naphthalene is boiled for a few minutes; if a solvent having a lower boiling point, such as xylene, is used, the reaction occurs more slowly and yields a mixture of phenanthroxazine and phenanthrazine. These results indicate that, in the formation of phenanthroxazine by the action of phenylhydrazine on phenanthraquinone (Bamberger and Grob, A., 1901, i, 280), the latter is first reduced to phenanthraquinol, which is transformed by the

action of ammonia into 9-amino-10-hydroxyphenanthrene, this then undergoing condensation to phenanthroxazine with elimination of water and ammonia :

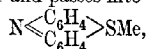


The action of aqueous ammonia on dihydroxyphenanthrene (Schmidt and Lumpp, A., 1910, i, 312; ii, 450; Foresti, this vol., ii, 524) yields first 9-amino-10-hydroxyphenanthrene, which gives (1) phenanthroxazine, and (2) diaminophenanthrene, which readily condenses to phenanthrazine.

T. H. P.

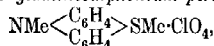
Sulphonium Bases Derived from Thiodiphenylamine and Analogous Substances. F. KEHRMANN and JEAN HENRI DARDEL (*Ber.*, 1922, 55, [B], 2346—2359; cf. A., 1918, i, 308, and previous abstracts).—The formation of sulphonium salts from aromatic sulphides containing a cyclic sulphur atom has been examined.

Thiodiphenylamine is obtained conveniently and in 82% yield by heating a mixture of diphenylamine and sulphur with a trace of iodine at 170°. It unites with methyl sulphate at 80° to yield the salt, $\text{NH} \langle \text{C}_6\text{H}_4 \rangle \text{SMe} \cdot \text{O} \cdot \text{SO}_3\text{Me}$, which is converted into the corresponding *perchlorate*, $\text{C}_{13}\text{H}_{12}\text{NSClO}_4$, a crystalline powder which is very unstable towards light. It is converted by sodium hydroxide solution into the colourless *base*, $\text{NH} \langle \text{C}_6\text{H}_4 \rangle \text{SMe} \cdot \text{OH}$, which readily loses water and passes into the *anhydride*,



an unstable, yellow substance which is reconverted by carbon dioxide into the colourless *carbonate* of the sulphonium type.

NS-Dimethylthiodiphenylaminesulphonium *perchlorate*,



colourless, thin prisms, is prepared in an analogous manner from methylthiodiphenylamine. The corresponding free *base* is colourless and soluble in water; it does not yield an anhydride, but is decomposed in hot solution into methyl alcohol and the methylated original material.

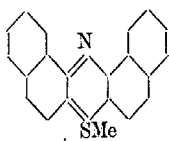
Thiophenyl-β-naphthylamine, sulphur-yellow needles, m. p. 178°, is obtained in 80% yield by heating phenyl-β-naphthylamine and sulphur with iodine at 200°/12—15 mm. It is converted in the usual manner into S-methylthiophenyl-β-naphthylaminesulphonium *perchlorate*, $\text{NH} \langle \text{C}_{10}\text{H}_6 \rangle \text{SMe} \cdot \text{ClO}_4$, colourless, lustrous needles (the corresponding yellow *picrate* and colourless *ferrocyanide* are described). It is transformed by sodium hydroxide into a yellow

base which could not be obtained in a homogeneous condition, but appears to be an anhydride. *NS-Dimethylthiophenyl-β-naphthylaminesulphonium perchlorate* is a colourless, crystalline powder which is not affected by cold sodium hydroxide solution, but is decomposed by warm alkali into methylthiophenyl-β-naphthylamine. *S-Methylthiophenyl-α-naphthylaminesulphonium perchlorate* is decomposed by sodium carbonate solution with separation of a yellow *anhydride*. Attempts to obtain a *N*-methylated thiophenyl-α-naphthylamine were unsuccessful.

Thiodi-β-naphthylamine, pale yellow needles, m. p. 233°, is readily prepared in 85% yield by heating a mixture of di-β-naphthylamine and sulphur with a little iodine at 180–200°. It is transformed in the usual manner into *S-methylthiodi-β-naphthylaminesulphonium perchlorate*, $\text{NH} \langle \text{C}_{10}\text{H}_6 \rangle \text{SMe} \cdot \text{ClO}_4$, a colourless, crystalline powder (the corresponding *chloride*, colourless leaflets, *platinichloride*, and *picrate* are described). The salts are converted by sodium hydroxide solution into the corresponding *anhydride* (annexed formula), pale orange-coloured needles, m. p. 160–165° (partial decomp.), which is reconverted by acids (including carbon dioxide) into colourless sulphonium salts. *NS-Dimethylthiodi-β-naphthylaminesulphonium perchlorate*, $\text{NMe} \langle \text{C}_{10}\text{H}_6 \rangle \text{SMe} \cdot \text{ClO}_4$, colourless crystals, is not decomposed by cold sodium hydroxide solution, but is converted by the hot reagent into *N*-methylthiodi-β-naphthylamine.

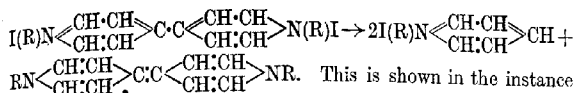


Thiodi-α-naphthylamine is obtained in 60–70% yield by heating a mixture of di-α-naphthylamine, sulphur, and a little iodine at 155–180°, and is conveniently purified through the black, crystalline *picrate*. It is transformed in the usual manner into *S-methylthiodi-α-naphthylaminesulphonium perchlorate*, a colourless, crystalline powder from which the corresponding *anhydride* (annexed formula), golden-yellow needles, m. p. 141°, is obtained. The latter substance is relatively stable towards dry air, but readily absorbs acid vapours with formation of colourless sulphonium salts.



H. W.

1 : 1'-Dialkyltetrahydro-4 : 4'-dipyridyls. BRUNO EMMERT and OTTO VARENKAMP (*Ber.*, 1922, 55, [B], 2322–2326; cf. A., 1920, i, 331; this vol., i, 680).—The recent observations of Dimroth and Frister (this vol., i, 678), that 1 : 1'-diacetyltetrahydro-4 : 4'-dipyridyl and 4 : 4'-dipyridyl react in acetic anhydride solution to form pyridine and diacetyldihydrodipyridyl, render it probable that dialkyltetrahydrodipyridyls could be converted by 4 : 4'-dipyridyldialkylidides into 1 : 1'-dialkylidihydrodipyridyls in accordance with the scheme : $\text{RN} \langle \text{CH} : \text{CH} \rangle \text{CH} : \text{CH} \langle \text{CH} : \text{CH} \rangle \text{NR} +$



This is shown in the instance of dibenzyltetrahydro-4:4'-dipyridyl and 4:4'-dipyridyl dibenzyl iodide to be the case; benzylpyridinium iodide is produced, but the second product is a merquinonoid substance formed by the union of molecular proportions of dibenzylidihydrodipyridyl and dipyridyl dibenzyl iodide.

1:1'-Dibenzyltetrahydro-4:4'-dipyridyl is conveniently prepared by the addition of sodium amalgam to a solution of benzylpyridinium chloride in water covered with a layer of ether in an atmosphere of hydrogen. When dissolved in ethyl alcohol and gradually treated with an aqueous solution of dipyridyl dibenziodide in an atmosphere of hydrogen, it gives benzylpyridinium iodide and the *quinhydrone*, $C_{48}H_{44}N_4I_2$, a dark violet powder, m. p. 180–185°, when rapidly heated, which is relatively stable towards air and dissolves in alcohol, aniline, pyridine, or acetic anhydride with the formation of dark blue solutions which become brown on exposure to air. It is prepared more conveniently, but in a less pure condition, by the action of a large excess of sodium amalgam on an aqueous solution of dipyridyl dibenzyl iodide. II. W.

Formaldehyde Derivatives of 2:5-Diketopiperazine. EMILE CHERBULEZ and EMANUEL FEER (*Helv. Chim. Acta*, 1922, 5, 678–687).—Protein substances are known to form compounds with formaldehyde, and it is suggested that combination takes place at the *N*-substituted amido-groups characteristic of these substances. To test this hypothesis, experiments have been made with 2:5-diketopiperazine, which is the simplest derivative of an α -amino-acid containing nitrogen only in the form of a substituted acid amide. 2:5-Diketopiperazine readily combines with formaldehyde to give 2:5-diketo-1:4-di-hydroxymethylpiperazine, small, colourless prisms, m. p. 178° (decomp.). It is a relatively stable substance forming a neutral aqueous solution, but dissolving more readily, without decomposition, in aqueous alkali. Its constitution is established by the preparation from it of the known 2:5-diketo-1:4-dibenzylpiperazine. It can be methylated with methyl sulphate to form 2:5-diketo-1:4-di-methoxymethyl-2:5-piperazine, colourless spangles, m. p. 99–100°, which is perfectly stable in aqueous solution. Benzoylation is best carried out with benzoic anhydride in pyridine; 2:5-diketo-1:4-di-benzoylmethylpiperazine forms brilliant spangles, m. p. 182°. With piperidine, diketodi-hydroxymethylpiperazine condenses to give 2:5-diketo-1:4-di-piperidinomethylpiperazine, long prisms, m. p. 156–157°, readily hydrolysed by hot water to diketopiperazine, formaldehyde, and piperidine.

By the action of phosphorus pentachloride on the diketodi-hydroxymethylpiperazine, 2:5-diketo-1:4-di-chloromethylpiperazine is formed, m. p. about 162° (decomp.). The chlorine atoms of this compound are extraordinarily reactive, in consequence of which

derivatives are formed with the greatest ease. The compound is decomposed by water with regeneration of the di-hydroxymethyl-compound, whilst with alcohols the alkoxy-derivatives are formed; 2 : 5-diketo-1 : 4-diethoxymethylpiperazine forms rhombic crystals, m. p. 92—93°. By the Friedel-Crafts' reaction with benzene, it gives 2 : 5-diketo-1 : 4-dibenzylpiperazine, and when heated alone with naphthalene, or with the addition of a little copper, at 150—160°, it condenses to form 2 : 5-diketo-1 : 4-di-naphthylmethylpiperazine, a white, crystalline powder, m. p. 189—192°. With β -naphthol, the dichloro-compound readily condenses, giving 2 : 5-diketo-1 : 4-di-(β -hydroxy- α -naphthylmethyl)piperazine, a crystalline powder, m. p. 285—286°; the dibenzoyl derivative forms fine needles, m. p. 267—268°.

E. H. R.

Preparation of Aromatic Selenium Compounds. FARRERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 348906 and 350376; from *Chem. Zentr.*, 1922, iv, 46).—An earlier patent (A., 1918, i, 218) is modified by using selenic acid instead of selenium or selenium dioxide and by substituting other solvents for sulphuric acid or working in the absence of solvents. The compound obtained from o-nitrophenol and selenic acid in the presence of sulphuric acid, is a yellow powder containing 16% of selenium, and exploding on heating. Antipyrine gives with selenic acid a compound containing 17% of selenium; it forms small crystals, m. p. about 238°, with discoloration. By the action of selenious oxide on p-nitroantipyrine in formic acid solution, di-p-nitroantipyril selenide is obtained; it forms yellow crystals, m. p. about 260° (decomp.). Di-p-tolylantipyril selenide, $(C_{12}H_{13}ON_2)_2Se$, prepared from p-tolylantipyrine and selenious acid in alcoholic solution, forms colourless crystals, m. p. about 255° (decomp.). The compound obtained by the action of selenious acid on resorcinol in aqueous solution is a brown powder.

G. W. R.

Preparation of Water-soluble Compounds of Diethylbarbituric Acid and its Homologues. JOHANN A. WÜLFING (D.R.-P. 345361; from *Chem. Zentr.*, 1922, ii, 1080—1081).—Solutions of diethylbarbituric acid or its homologues are treated with the theoretical amount of calcium hydroxide, magnesium hydroxide, or freshly precipitated calcium carbonate, if necessary with heating, and after filtration, if required, evaporated to dryness in a vacuum. The calcium salt and the magnesium salt of diethylbarbituric acid are mentioned, and also the calcium salt and the magnesium salt of phenylethylbarbituric acid. The products have therapeutical uses and form stable mixtures with alkaline earth salts of o-acetoxybenzoic acid.

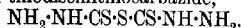
G. W. R.

3-Hydroxy-2-phenylindazole. GUSTAV HELLER (*Ber.*, 1922, 55, [B], 2680).—In reply to von Auwers and Hüttenes (this vol., i, 682), the author maintains the individuality of the isomeric form of 3-hydroxy-2-phenylindazole described by him (A., 1917, i, 219).

H. W.

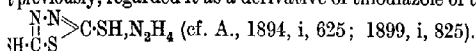
The Interaction of Aniline and Acraldehyde. FREDERICK GEORGE MANN (T., 1922, 121, 2178—2182).

Dithiocarbazinic Acid. II. SIMA M. LOSANITCH (*Glas. Acad. Sci. Belgrade*, 1922, 103, 1—9).—In a previous communication T., 1921, 119, 763), it was shown that the dithiocarbazates decompose slowly when heated in aqueous or alcoholic solution, yielding hydrogen sulphide, ammonium sulphide, ammonia (or an amine), sulphur, and a white, crystalline product of acid reaction. This decomposition yields in the beginning hydrogen sulphide, emithiocarbazide, and thiocarbazide. Subsequently, the products of the first decomposition interact with the dithiocarbazinate and form ammonia and thiodisemithiocarbazide,



The latter product then suffers transformation into the white, crystalline acid product mentioned in the first communication. For this compound the author suggests the constitution

$\text{S}(\text{C}(\text{SH}) \cdot \text{N} \cdot \text{NH}_2)_2$, or $\text{S}(\text{C} \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{NH}_2)_2$, whilst Busch, who obtained it previously, regarded it as a derivative of thiodiazole of the formula



It forms colourless needles and plates, decomp. about 170°, m. p. 225°, and is soluble in water, less so in alcohol. With methyl iodide, it yields a *dimethyl* ester, colourless crystals, m. p. 136—137°. It also forms a mono-, di-, and poly-sulphide. The disulphide has been already described by Ziegele (A., 1899, i, 827). The *monosulphide* is formed if the aqueous or alcoholic solution of the acid is boiled; it crystallises in yellow needles, m. p. 178° (decomp.), and forms salts with bases. The salts of the alkalis and ammonium are soluble in water; those of the heavy metals insoluble. The ammonium salt yields with methyl iodide the *monosulphide methyl* ester, a white substance, soluble in alcohol; m. p. 71°. The *polysulphide*, $\text{C}_4\text{H}_4\text{N}_4\text{S}_7$, is formed together with the disulphide by the method employed by Ziegele (*loc. cit.*); it is insoluble even in boiling alcohol, forms yellow crystals, m. p. 186°, and is not identical with the polysulphide ($\text{C}_2\text{H}_2\text{N}_2\text{S}_3$) described by Ziegele. S. S. M.

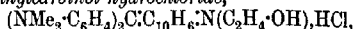
The Cyanine Dyes. VI. Dyes containing a Quinoline and a Benzothiazole Nucleus. The Thioisocyanines. WALTER THEODORE KARL BRAUNHOLTZ and WILLIAM HOBSON (T., 1922, 121, 2004—2008).

Formation of Triphenylpararosanine Hydrochloride from Diphenylamine and Chloralammonia. RIKI HORIUCHI (*Mem. Coll. Sci. Kyoto*, 1921, 5, 1—7).—The small yield of triphenylpararosanine hydrochloride obtained by heating diphenylamine and chloralammonia directly at 130°, is greatly increased by maintaining the temperature at 100° for some time prior to heating at 130°. The author has investigated the reaction of diphenylamine with various compounds containing CCl_2 and CHO groups, respectively, and concludes that compounds containing the former

group are alone concerned in the formation of diphenylamine-blue, the chlorine atoms being replaced by the phenyl group, and the resulting product reacting with part of the hydrogen chloride produced.

J. S. G. T.

Preparation of New Triarylmethane Colouring Matters. BRITISH DYESTUFFS CORPORATION, LTD., ARTHUR GEORGE GREEN, KENNETH HERBERT SAUNDERS, and STANLEY CHARLES BATE (Brit. Pat. 185612).—New triarylmethane dyes containing an hydroxyalkyl group attached to nitrogen are obtained by condensing Michler's ketone or Michler's hydrol with an arylhydroxyalkylamine, an arylidihydroxyalkylamine, an arylalkylhydroxyalkylamine, or an arylaralkylhydroxyalkylamine, and, where the hydrol is used, oxidising the leuco-compound first produced to the dyestuff in the usual way. For example, *tetramethylethanoltriaminodiphenyl* *naphthylcarbinol hydrochloride*,



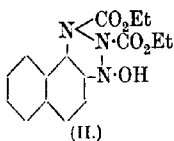
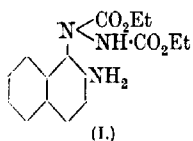
is obtained by adding 23 parts of α -naphthylethanolamine to the product of the action of 20 parts of phosphorus oxychloride on 30 parts of tetramethyldiaminodiphenyl ketone in presence of toluene as diluent. The dye crystallises on cooling in green crystals, which have the same properties as Victoria-Blue-R except that the solubility is much superior. *Tetramethyldiethanoltriaminodiphenyl* *naphthylcarbinol hydrochloride*,



prepared from Michler's hydrol and diethanolaniline, and subsequent oxidation of the resulting leuco-compound with lead peroxide, is a coppery powder which dyes tanned cotton bright purple shades. Other shades of purple are obtained by substituting for the diethanolaniline other hydroxyalkylarylamines such as ethanolaniline, diethanol-*o*-toluidine, etc.

G. F. M.

The Structure of the Compounds Obtained by the Oxidation of the Additive Products of β -Naphthylamine and Azocarbonyl Esters. OTTO DIELS and HARALD WACKERMANN (*Ber.*, 1922, 55, [B], 2443—2450).—The additive compound of β -naphthyl-

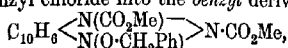


amine and ethyl azodicarboxylate (annexed formula I) has been observed to be converted by oxidation into a yellow compound to which the formula II

has been assigned (cf. A., 1921, i, 280). The correctness of the second formula is established by a series of experiments starting from the corresponding methyl ester.

The compound $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N}(\text{CO}_2\text{Me}) \\ \text{N}(\text{OH}) \end{smallmatrix} \text{CO}_2\text{Me}$, brownish-yellow prisms, m. p. 117° (decomp.), is prepared by the addition of hydrogen peroxide to a hot solution of the additive compound of β -naphthylamine and methyl azodicarboxylate in glacial acetic acid. The presence in it of a mobile hydrogen atom is established

by the formation of an additive compound, $C_{15}H_{18}O_8N_4$, m. p. 138° , with carbethoxycarbimide and by its conversion by potassium ethoxide and benzyl chloride into the benzyl derivative,



colourless crystals, m. p. 187° . Cautious treatment of the product of the oxidation of the methyl or ethyl ester with dilute alkali hydroxide solution causes hydrolysis, loss of carbon dioxide, and formation of the acid, $C_{10}H_6 \begin{array}{c} \text{NH} \\ \text{N}(\text{OH}) \end{array} \text{N} \cdot \text{CO}_2\text{H}$, pale yellow needles,

m. p. 128° ; the alternative formula, $C_{10}H_6 \begin{array}{c} \text{N}(\text{CO}_2\text{H}) \\ \text{N}(\text{OH}) \end{array} \text{NH}$, is excluded since the acid does not immediately lose water and carbon dioxide with the formation of 1:2-azimidonaphthalene. The latter substance, m. p. $178-179^\circ$, is, however, produced when the acid is treated with methylamine (40%).

A similar conclusion is drawn from an attempt to obtain the methyl ether of the oxidation product by means of diazomethane; normal methylation appears to take place in the first instance, but the methyl ether is unstable, immediately losing carbon dioxide and, presumably, dimethyl ether with consequent formation of methyl $\alpha\beta$ -aziminonaphthalenecarboxylate, $C_{10}H_6 \begin{array}{c} \text{N}(\text{CO}_2\text{Me}) \\ \text{N} \end{array} \text{N}$, pale, reddish-brown prisms, m. p. $132-133^\circ$; the identity of the latter compound is established by its production from aziminonaphthalene and methyl chloroformate in the presence of benzene and pyridine.

H. W.

Addition of Azoimide at Contiguous Double Linkings.

VIII. 5-Anilino-1-phenyltetrazole and the Azide of Dithiocarbamic Acid. E. OLIVERI-MANDALÀ (*Gazzetta*, 1922, 52, ii, 139-144; cf. A., 1913, i, 961).—The action of azoimide on carbodiphenyldi-imide yields 5-anilino-1-phenyltetrazole, $\text{N} \begin{array}{c} \text{N} \cdot \text{NPh} \\ \text{N} \cdot \text{C} \cdot \text{NHPh} \end{array}$, which forms slender, white, acicular crystals,

m. p. 162° , and yields an acetyl compound, m. p. 87° , and a silver derivative, $C_{13}H_{10}N_5\text{Ag}$. This compound, which is undoubtedly formed by way of the azide, $\text{NPh} \cdot \text{C} \cdot \text{NPh} + \text{N}_3\text{H} \rightarrow \text{NPh} \cdot \text{C}(\text{N}_3) \cdot \text{NHPh} \rightarrow C_{10}H_{11}N_5$, is identical with that obtained by Busch and Bauer (A., 1900, i, 414) by the action of nitrous acid on aminodiphenylguanidine and regarded by these authors as phenyliminophenyldihydrotetrazole, $\text{N} \begin{array}{c} \text{N} - \text{NPh} \\ \text{NH} \cdot \text{C} \cdot \text{NPh} \end{array}$; from its mode of preparation, its

marked stability towards concentrated solutions of acids and bases, and its formation of an acetyl derivative, the compound must, however, be regarded as a tetrazole derivative, although it is not improbable that in the formation of salts it may undergo transformation into the phenyliminophenyltetrazolone. When heated above its melting point, 5-anilino-1-phenyltetrazole decomposes, yielding carbylamine, azoimide, and 1-phenyltetrazole, m. p. 65° (Freund and Paradies, A., 1901, i, 770; Oliveri-Mandalà and

Alagna, A., 1911, i, 243), the last resulting from the interaction of the phenylcarbylamine and azoimide.

Azoimide combines also with carbon disulphide giving an explosive compound, which corresponds in behaviour with the azides of thiocarbamic acids and has probably the structure, $\text{SH}\cdot\text{CS}\cdot\text{N}_3$. It forms a sodium salt, $\text{CN}_3\text{S}_2\text{Na}$, and when heated gently with dilute hydrochloric acid decomposes losing two atoms

of nitrogen and one atom of sulphur, $\text{SH}\cdot\text{CS}\cdot\text{N}_3 \rightarrow \begin{smallmatrix} \text{S} \\ \diagup \text{N} \diagdown \end{smallmatrix} \text{C}\cdot\text{SH} \rightarrow$

$\text{HS}\cdot\text{C}\cdot\text{N}$, and, if concentrated solutions are used, yields the insoluble, yellow compound, $\text{C}_2\text{H}_2\text{N}_2\text{S}_3$, obtained on decomposition of aqueous thiocyanic acid solutions. Some of the salts of the explosive azide were prepared by Sommer (A., 1916, ii, 29).

The above results, together with those published in the author's previous papers, show (1) that with carbylamines, ketens, esters of isocyanic and thiocyanic acids, carbodiphenyldi-imide and carbon disulphide, which contain two contiguous double linkings, azoimide readily unites, the triazo-group becoming attached always to the carbon atom and the hydrogen to the nitrogen atom; that, in the first two cases, integral addition of the azoimide molecule to the double linking may result in the formation of tetrazole derivatives. (2) That the unsaturated groupings, $\cdot\text{N}\cdot\text{C}(\text{N}_3)\cdot$ and $\cdot\text{C}\cdot\text{C}(\text{N}_3)\cdot$, undergo rapid isomerisation to the corresponding heterocyclic compounds, $\text{N}\begin{smallmatrix} \diagup \text{N} \diagdown \\ \text{C} \end{smallmatrix}$ and $\text{N}\begin{smallmatrix} \diagup \text{C} \diagdown \\ \text{N} \end{smallmatrix}$. The only known compound

of this type with which isomerisation of the triazo-group does not occur is vinylazoimide (Forster and Newman, T., 1910, 97, 2570), which does not undergo isomeric change to isotriazole. On account of the ease with which the three nitrogen atoms, even when forming part of a nucleus, are eliminated as azoimide, the compound described by Thiele and Ingle (A., 1896, i, 107) as tetrazylazoimide



must be regarded as composed of two tetrazole nuclei (annexed formula). (3) That diphenylcarbodi-imide reacts more readily than phenylcarbimide with azoimide. This is in accordance with the observations of Staudinger and Meyer (A., 1920, i, 228), who found that replacement of the carbonyl group in $\text{NPh}_2\text{C}=\text{O}$ by $\text{C}(\text{NPh})_2$ causes marked increase in the reactivity. T. H. P.

The Influence of Hydrogen-ion Concentration on the Solubility of Uric Acid. A. JUNG (*Helv. Chim. Acta*, 1922, 5, 688—702).—Experiments were made to determine whether slight changes in the degree of acidity in the neighbourhood of the neutral point, such as can be obtained by the use of buffer systems, have any influence on the solubility of uric acid. It is found that the influence is considerable. The solubility is lowest with low p_{H} values, that is, in acetate mixtures, and highest in phosphate and borate mixtures. It rises from 0.59 gram per litre at p_{H} 7.09 to 1.54 grams per litre at p_{H} 7.6, and continues to rise rapidly above this p_{H} value. It appears probable that the character of the anion in the buffer salt has a chemical influence; complex

salts may be formed, for instance, between the uric acid and borates or phosphates. In the case of all solutions having a p_H value higher than 7.6, when the saturated solution was kept for fourteen days almost the whole of the uric acid was precipitated. This precipitate may be a complex salt or may be sodium biurate precipitated through decomposition of a complex compound. Uric acid is completely precipitated from solution by animal charcoal, and since at the same time there is generally a slight fall in the p_H value of the solution, it appears that uric acid salts are adsorbed by the charcoal.

E. H. R.

Preparation of Carboxylic Acids of the Purine Series.

E. MERCK, OTTO WOLFES, and ERICH KORNICK (D.R.-P. 352980; from *Chem. Zentr.*, 1922, iv, 160—161).—Salts of mono- or dialkylated xanthines are treated with salts of monohalogenated aliphatic carboxylic acids. By heating sodium theobromine in aqueous alkaline solution with monochloroacetic acid, *theobromine-1-acetic acid* is obtained as colourless crystals, m. p. 260°. Theophylline and monochloroacetic acid give *theophylline-7-acetic acid*, crystals, m. p. 271° (corr.). 3-Methylxanthineacetic acid forms needles, m. p. 306° (decomp.). Sodium 3-methylxanthine and β -iodopropionic acid give *3-methylxanthinepropionic acid*, lustrous leaflets, m. p. 308—309° (decomp.). The *N*-alkyl-carboxylic acids of mono- and di-alkyl xanthines and their salts have therapeutic uses.

G. W. R.

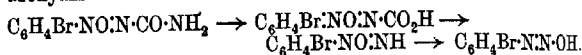
Azoxyamides and Diazo-compounds. A. PIERONI (*Gazzetta*, 1922, 52, ii, 32—43).—Since only one phenylazoxycarbonamide is obtainable from phenylazocarbonamide, although Angeli's results (A., 1916, i, 679) indicate that two isomerides should exist, the author has investigated *p*-bromo- and *p*-nitro-phenylazocarbonamides and the corresponding azoxy-derivatives. For the preparation of these azocarbonamides, Widman's general method (A., 1895, i, 603) yields unsatisfactory results. *p*-Bromophenylazocarbonamide may, however, be obtained by diazotising *p*-bromoaniline, treating the diazonium salt with aqueous potassium cyanide solution, and treating the nitrile thus formed in moist ethereal solution with a current of hydrogen chloride; under these conditions, the nitrile unites with a molecule of water. The compounds thus obtained, namely, *p*-bromo-, *p*-nitro-, and 2:4-dibromophenylazocarbonamides, and *p*-bromo- and *p*-nitro-phenyldiazonitriles, were subjected to the action of hydrogen peroxide in acetic acid solution. Of the azoxyamides prepared in this way, none could be obtained in two isomeric forms, and the method of formation and also the behaviour indicate in all cases the formula $O\cdot N\cdot R\cdot N\cdot CO\cdot NH_2$; that they are not more complex compounds is shown by their cryoscopic behaviour. The constitution of *p*-bromophenylazoxycarbonamide is confirmed by the readiness with which it is reduced, by means of zinc dust and acetic acid, to the original azocarbonamide. Treatment of aqueous *p*-bromophenylazoxycarbonamide with an alkaline solution of potassium hypobromite

and subsequently with β -naphthol results in evolution of gas and formation of bromophenylazo- β -naphthol-red.

The fact that *p*-bromo- and *p*-nitro-benzodiazonitriles are oxidised by hydrogen peroxide in acetic acid solution, yielding mainly the corresponding azoxyamides, indicates that the action of hydrogen peroxide on *p*-chlorobenzodiazonitrile proceeds, not in the manner supposed by Bamberger and Baudisch (A., 1912, i, 733), but in the two stages described by Angeli (*loc. cit.*): $C_6H_4Cl \cdot N \cdot N \cdot CN + H_2O_2 = C_6H_4Cl \cdot NO \cdot N \cdot CN + H_2O$ and $C_6H_4Cl \cdot NO \cdot N \cdot CN + H_2O = C_6H_4Cl \cdot NO \cdot NOH + HCN$.

Under the ordinary experimental conditions, 2:4-dibromophenylazocarbonamide is not oxidised to the corresponding azoxy-derivative by hydrogen peroxide, and no azoxy-compound has been obtainable from benzoylazo-*p*-bromobenzene.

All the azoxyamides obtained exhibit close analogy to aromatic diazo-compounds. In slightly alkaline solution, they react with β -naphthol to give the corresponding benzeneazonaphthols, and they also react in alkaline solution with pyrrole and its derivatives, with phenols, with ethyl acetoacetate, and with nitroethane. With saturated aqueous potassium hydroxide solution, the *p*-bromo-azoxyamide reacts in accordance with the scheme:



Since the two isomerides, $O \cdot NPh \cdot N \cdot C_6H_4 \cdot OH$ and $NPh \cdot NO \cdot C_6H_4 \cdot OH$,

yield the compound $NPh \cdot N \cdot OH$ as final product when oxidised with permanganate, and since also the nitrosoamine of phenyl-carbamide, $NH_2 \cdot CO \cdot NPh \cdot NO$, which is isomeric with phenylazoxycarbonamide, reacts in alkaline solution with β -naphthol like diazo-derivatives and azoxyamides, giving phenylazonaphthol, the existence of the two isomerides $O \cdot NPh \cdot NH$ and $NPh \cdot NH \cdot O$ may be assumed. The normal diazotates will therefore be represented by the general formulæ $O \cdot NR \cdot NH$ and $NR \cdot NH \cdot O$ (cf. Angeli, A., 1916, i, 679), and the behaviour of these compounds is explained better by the presence of conjugated double linkings than by Hantzsch's view that normal and iso-diazotates are spacial isomerides of the formula, $NR \cdot N \cdot OH$.

Phenylazoxycarbonamide, $O \cdot NPh \cdot N \cdot CO \cdot NH_2$, forms long needles, m. p. 150° (decomp.), reddening in the air, and exhibits normal cryoscopic behaviour in acetic acid solution.

2:4-Dibromophenylazocarbonamide, $C_6H_3Br_2 \cdot N \cdot N \cdot CO \cdot NH_2$, crystallises in long, orange-yellow, silky needles, m. p. 194°.

p-Bromophenylazocarbonamide, $C_6H_4Br \cdot N \cdot N \cdot CO \cdot NH_2$, forms crystals, m. p. 175° (decomp.).

p-Bromophenylazoxycarbonamide, $C_6H_4Br \cdot NO \cdot N \cdot CO \cdot NH_2$, crystallises in pale yellow needles, m. p. 201° (decomp.).

p-Nitrophenylazoxycarbonamide, $C_6H_4O_2 \cdot N \cdot N$, forms pale yellow needles, m. p. 203° (decomp.), and readily undergoes change owing to the presence of the nitro-group, which tends to expel the less highly negative and less stable azoxy-group. With β -naphthol in

alkaline solution, the amide readily reacts with formation of the deep red *p*-nitrophenylazo- β -naphthol.

Potassium *p*-bromobenzeneazoxycarboxylate, $C_6H_4Br \cdot NO \cdot N \cdot CO_2K$, is a yellow, crystalline compound, but could not be obtained pure, as it readily undergoes alteration.

T. H. P.

Certain Salts with para-, ortho-, and meta-Quinonoid Structure. III. R. CIUSA and G. RASTELLI (*Gazzetta*, 1922, 52, ii, 121—125; cf. A., 1920, i, 256; 1921, i, 63).—The authors have completed the optical investigation of *p*- and *o*-nitrophenylhydrazones and the corresponding alkali metal salts.

The monosodium salt of pyruvic acid *p*-nitrophenylhydrazone, $CO_2Na \cdot CMe \cdot N \cdot NH \cdot C_6H_4 \cdot NO_2$, forms lustrous, pale yellow scales; the monopotassium salt, similar scales; the disodium salt, small, violet crystals, and the dipotassium salt, small, violet needles. All these salts yield the original hydrazone on hydrolysis.

Pyruvic acid *o*-nitrophenylhydrazone forms yellow needles, m. p. 221°, the mono-sodium and potassium salts yellow scales, and the di-sodium and potassium salts blue crystals with metallic lustre; these salts also give the original hydrazone when hydrolysed.

Solutions of these quinone-nitronic acids are moderately stable, and in the experimental conditions employed obey Beer's law sufficiently well. Spectrographic examination shows that the salification is accompanied by profound structural change; the benzenoid form of benzaldehyde-*p*-nitrophenylhydrazone is altered to a para-quinonoid structure, the characteristic band at 2100, which is shown by ordinary quinone, becoming evident. Similarly, pyruvic acid *p*-nitrophenylhydrazone and its monometallic salts are benzenoid, and its dimetallic salts quinonoid, in character. The *o*-nitrophenylhydrazones exhibit the same behaviour.

T. H. P.

Certain Salts with para-, ortho-, and meta-Quinonoid Structure. IV. R. CIUSA and G. RASTELLI (*Gazzetta*, 1922, 52, ii, 126—128; cf. preceding abstract).—The action of methyl iodide on the potassium salt of benzaldehyde-*p*-nitrophenylhydrazone yields, not a quinonoid methyl ether of the hydrazone, but benzaldehyde-*p*-nitrophenylmethylhydrazone, $CHPh \cdot N \cdot NMe \cdot C_6H_4 \cdot NO_2$, which separates in either red or canary-yellow crystals, m. p. 131°, yields *as-p*-nitrophenylmethylhydrazone on hydrolysis, exhibits an absorption spectrum similar to that of benzaldehyde-*p*-nitrophenylhydrazone, and in acetone solution gives no coloration with alkali.

as-p-Nitrophenylmethylhydrazine, $NH_2 \cdot NMe \cdot C_6H_4 \cdot NO_2$, forms yellowish-brown, acicular crystals or silky, yellow needles, m. p. 156°, reduces Fehling's solution, gives a silver mirror with ammoniacal silver nitrate, and condenses with aldehydes and ketones to the corresponding hydrazones. This constitution was suggested by Charrier (A., 1915, i, 905) for a compound, m. p. 142°. The hydrazine forms a *picrate*, $NH_2 \cdot NMe \cdot C_6H_4 \cdot NO_2 \cdot C_6H_3O_2N_3$, m. p. 131° (decomp.), and with ferric chloride solution yields a small proportion of a compound, m. p. 145—146°, which is possibly the corresponding tetrazene.

VOL. CXXII. i.

p p

Pyruvic acid as p-nitrophenylmethylhydrazone forms both red and yellow modifications, m. p. 153°.
T. H. P.

Protein Precipitants. ALMA HILLER and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1922, **53**, 253—267).—With the object of ascertaining the extent to which proteins and protein products are precipitated by different protein precipitants, the action of a number of these substances both on blood and Witte's peptone has been studied. The results with the latter substance indicate that tungstic acid and picric acid precipitate protein intermediate products relatively completely without precipitating the amino-acids; trichloroacetic acid removes proteins only, nearly all the protein products passing into the filtrate; whilst metaphosphoric acid, colloidal iron, and mercuric chloride occupy an intermediate position with regard to their action on protein products. With blood, all the substances studied removed proteins completely, and all, with the exception of alcohol, allowed similar amounts of amino-acids to pass into the filtrates. The recovery of added mixed monoamino-acids was, however, incomplete in the cases of metaphosphoric acid and alcohol.
E. S.

The Colloidal Behaviour of Serum Globulin. DAVID I. HITCHCOCK (*J. Gen. Physiol.*, 1922, **5**, 35—44).—The globulin of ox serum behaves stoicheiometrically as an amphoteric electrolyte, like other proteins which have been investigated, such as gelatin. The potential differences and osmotic pressures across membranes separating acid solutions of this protein from water are largely explicable by Donnan's theory of membrane equilibrium.
W. O. K.

Effect of Acids and Alkalis on some Chemical and Physical Properties of Hæmoglobin. G. QUAGLIARIELLO (*Arch. Sci. biol.*, 1921, **2**, 423—472; *Ber. ges. physiol.*, 12, 82—83; from *Chem. Zentr.*, 1922, iii, 52—53).—The author has studied the effect of lactic acid, hydrochloric acid, and sodium hydroxide on the surface tension of protein solutions, and in particular of hæmoglobin solutions, by stalagmometric measurements. The effect of lactic acid is similar to that of hydrochloric acid. Both acids and alkali exert the same effect on hæmoglobin solutions as on solutions of other protéins. No evidence was found for an aggregation of the hæmoglobin molecule. The surface tension, like the solubility, osmotic pressure, viscosity, and swelling power, shows a minimum at the isoelectric point, all these properties being connected with the degree of dissociation of the ampholyte. The free ions are hydrated more easily than the molecules. The marked depression of the surface tension at the isoelectric point appears abnormal, since the less stable is a colloidal solution the more does the surface tension approach that of the solvent. The lowering in concentration consequent on molecular aggregation must be balanced by increased surface activity.
G. W. R.

Hæmocyanin. VI and VII. The Action of some Gases on Hæmocyanin. CH. DÉRÉ and A. SCHNEIDER (*J. physiol. path. gén.*, 1922, **20**, 1—13; 34—40).—An examination of the action of

hydrogen, nitrogen, carbon dioxide, carbon monoxide, nitric oxide, methane, acetylene, and ethylene on hæmocyamin. The oxy-hæmocyamins from the various species used are as easily and rapidly reduced by treatment with an inert gas at 15° to 20° as by a vacuum at 40°. Hæmocyamin forms with nitric oxide a crystallisable, green pigment which is less unstable than oxyhæmocyamin. Reduced hæmocyamin at 20° does not form coloured compounds with methane, ethylene, or acetylene.

CHEMICAL ABSTRACTS.

Preparation and Analysis of Animal Nucleic Acid. P. A. LEVENE (*J. Biol. Chem.*, 1922, **53**, 441—447).—The author's method (A., 1921, i, 821) for the preparation of animal nucleic acid has been improved. The ground glands (10 lb.) are boiled for thirty-five minutes with 5 litres of water containing 250 grams of sodium hydroxide. The mixture is then neutralised with acetic acid, treated with a colloidal solution (50 c.c.) of iron, filtered, and left over-night. Addition of a double volume of methyl alcohol containing 2% of hydrochloric acid precipitates the nucleic acid. The method has been applied to thymus gland, spleen, kidney, pancreas, and liver. In the latter case, the product contains considerable amounts of glycogen and must be further purified. Nucleic acids from the above organs have the same elementary composition, which corresponds with that of a hexose tetranucleotide. Estimations of the purine bases also agree with the tetranucleotide theory.

E. S.

Some Properties of Dialysed Gelatin. DOROTHY JORDAN LLOYD (*Biochem. J.*, 1922, **16**, 530—540).—The influence of hydrochloric acid, sodium hydroxide, and sodium chloride on the gelling power of gelatin purified by dialysis at the isoelectric point (cf. A., 1920, i, 452, 895) has been followed. For comparative purposes, the minimum concentration of gelatin necessary to produce a gel after keeping for forty-eight hours at 15° has been taken as an inverse measure of the gelling power. Under these conditions, pure gelatin requires a minimum concentration of 0.8% to form a gel. Hydrochloric acid decreases the gelling power, the diminution passing through a maximum at P_H 2—3 and again beyond P_H 0.7. Sodium hydroxide slightly decreases the gelling power between P_H 10—12, and completely prevents gelation above P_H 12. Neutral salts diminish the influence of hydrogen ions on gelling power; no other simple relationship between sodium chloride content and gelling power appears to exist.

The influence of hydrochloric acid, sodium hydroxide, and sodium chloride on the production of turbid gels, and the effect of temperature on the optical rotation of gelatin have also been studied. Finally, the theory of gelation is discussed.

E. S.

Thermal Expansion of Gelatin Gels. ALAN TAFFEL (*T.*, 1922, **121**, 1971—1984).

Saccharase. E. CANALS (*Bull. Soc. chim.*, 1922, [iv], **31**, 921—923; cf. *Tribot*, A., 1909, i, 73).—An attempt to verify the author's hypothesis that magnesium behaves as a catalytic agent

with regard to saccharase in a manner analogous to that of manganese with regard to oxydases. Analysis of saccharases from various sources shows that all specimens contain a considerable proportion of magnesium and of phosphoric acid, similar results being obtained from a filtered solution made from each specimen. Other substances found in the ash are potassium, sodium, iron, aluminium, calcium, chlorine, and sulphur (as sulphate), but in some cases one or more of these elements are missing or present only in traces. The magnesium and phosphate content when examined quantitatively shows wide variation.

H. J. E.

A Silver Compound of Saccharase. H. VON EULER and K. JOSEPHSON (*Ber.*, 1922, 55, [B], 2416—2420).—Previous investigations on the inactivation of saccharase by silver salts (Euler and Svanberg, A., 1921, i, 68, 202; Euler and Myrbäck, this vol., i, 693) have made it very probable that a compound of saccharase and silver is formed; such a product has now been isolated in a somewhat impure condition.

A saccharase solution is concentrated in a vacuum until it is approximately 1% and treated with an excess of silver nitrate; after some hours, the solution becomes brown, but remains clear. Addition of concentrated alcohol causes the separation of a brown precipitate which can be readily removed by centrifuging; it is purified by solution in water and re-precipitation with alcohol. It contains approximately 50% of carbohydrates, which are derived mainly from the original yeast. Analysis of the product gives silver 2.5%, phosphorus 0.81%, nitrogen 4.5%, carbon 41.5%, hydrogen, 7.6%, and oxygen 43.1%. It is remarkable that the atomic ratio of phosphorus to silver is 1:1. This is in agreement with the value deduced from the experiments of Euler and Myrbäck (*loc. cit.*).

H. W.

The Inactivation of Saccharase by Iodine. H. VON EULER and STURE LANDERGREN (*Biochem. Z.*, 1922, 131, 386—389).—Addition of iodine in potassium iodide solution to two different saccharase preparations of different activity reduced the activity to one-half. Sodium thiosulphate cannot reactivate the saccharase.

H. K.

Effect of Filtration on Amylases. JEAN EFFRONT (*Compt. rend. soc. Biol.*, 1922, 86, 271—273; from *Chem. Zentr.*, 1922, iii, 177; cf. this vol., i, 184).—Ptyalin retained from saliva by filter-paper cannot be removed by water or by sugar solution. It is removable, however, in the presence of sodium chloride or starch paste. This absorption increases with rise of temperature and affects, not only diastases, but also inhibitory substances accompanying them. Diastases may thus be purified by filtration. Many inactive plant juices may be activated by filtration.

G. W. R.

Characteristic Properties of Amylases of Different Origin. JEAN EFFRONT (*Compt. rend. soc. Biol.*, 1922, 86, 274—275; from *Chem. Zentr.*, 1922, iii, 177; cf. preceding abstract).—Amylases

of animal origin, from bacteria, and from seeds are readily isolated by maceration. Amylases from green plant materials are isolated with difficulty, but more readily in the presence of sodium chloride or starch paste. Animal amylases, and amylases from germinated seeds quickly form sugar from starch grains, 72—74% being changed within an hour. Amylases from resting seeds and from vegetative portions of plants are less active. The optimum temperature for animal and bacterial amylases and for amylases from vegetative portions of plants is 40°. For amylases of certain germinated seeds, the optimum temperature is 60°. Resistance to heat and chemical effects (acids) varies with origin. G. W. R.

The Asymmetric Action of Emulsin in the Benzaldehyde-cyanohydrin Synthesis. E. NORDEFELDT (*Biochem. Z.*, 1922, 131, 390—410; cf. this vol., i, 66).—The author has made a detailed examination of the most favourable conditions for the formation of optically active cyanohydrin and records some properties of emulsin. For the production of optically active cyanohydrin, emulsin is necessary. With small quantities of emulsin, there is proportionality between the rotation attained and the amount of emulsin present, but with larger quantities the rotation rises more slowly than would be expected. The *d*-cyanohydrin is labile and its rotation falls off spontaneously. This velocity of autoracemisation increases with rise of temperature and with increasing acidity within the range P_H 3 to 6.5. At the neutral point the velocity of racemisation equals the velocity of formation of the cyanohydrin and the product is inactive. H. K.

Mechanism of Action of Oxidising and Reducing Ferments. F. BATTELLI and L. STERN (*Arch. internat. Physiol.*, 1921, 18, 403—418; *Ber. ges. Physiol.*, 1922, 11, 431—432; from *Chem. Zentr.*, 1922, i, 1203—1204).—Ferments are divided into three groups, according to the behaviour of the ions of water to the substrate, namely hydratases, for example, the ferment concerned in the reversible change fumaric acid to maleic acid; hydrolases producing esterification or hydrolysis; and oxydoreductases in which the hydrogen and hydroxyl ions of water give reduction and oxidation products respectively. Catalase is regarded as an oxydoreductase. G. W. R.

The Action of Poisons on Enzymic Processes. VII. Metal Catalysis and Catalase Action. VIII. The Volumetric Method for the Estimation of Catalase. C. G. SANTESSON (*Skand. Arch. Physiol.*, 1922, 47, 129—181, 191—208).—VII.—The amount of catalyst is of importance when the material acted on is constant; colloidal metals in minute amounts are often ineffective. Frog muscle catalase shows similar properties, although not so regularly; the effective amount of catalase may be of the order 0.06 mg. A low temperature (0.6—0.9°) markedly decreases the evolution of oxygen caused by colloidal silver; heating the solution also inhibits its activity. Muscle catalase is similarly affected. The effect of a series of ions on the activity of colloidal silver and muscle catalase is widely different in the two cases.

VIII.—A criticism of the methods available for the determination of catalase activity. The use of 0.211% (0.062*N*) hydrogen peroxide is preferred.

CHEMICAL ABSTRACTS.

The Anaerobic and Aerobic Oxidation of Xanthine and Hypoxanthine by Tissues and by Milk. E. J. MORRIS, C. P. STEWART, and F. G. HOPKINS (*Proc. Roy. Soc.*, 1922, [B], 94, 109—131).—Milk and certain animal tissues contain a catalytic system which can bring about the rapid oxidation of xanthine and hypoxanthine to uric acid either anaerobically in the presence of methylene-blue (which is thereby reduced), or aerobically in its absence. The action of the enzyme is highly specific; thus, neither guanine, caffeine, theobromine, uracil, thymine, cytosine, nor histidine is able to induce the reduction of methylene-blue in milk. Adenine does so slowly, but this is due to the presence of adenase, which converts the adenine into hypoxanthine. Under anaerobic conditions uric acid is produced at the same rate from both xanthine and hypoxanthine; when aerobic conditions prevail, however, the time required for the complete conversion of hypoxanthine into uric acid is twice that necessary in the case of xanthine. This is probably due to the fact that the system is homogeneous in the former, and heterogeneous in the latter, case. With moderate concentrations of base present the oxidation proceeds at a linear rate.

E. S.

Enzyme Action. XXIII. Homo- and Hetero-lytic Enzymes. HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1922, [B], 94, 132—133).—The author considers that the conversion of xanthine and hypoxanthine into uric acid by the milk enzyme (cf. preceding abstract) is a hydrolytic change. The action of the enzyme differs from that of ordinary hydrolytic enzymes, which induce the distribution of the elements of water between two sections of a single molecule, in that these elements are distributed between two distinct molecules. It is suggested that the terms *homo-* and *hetero-lytic* be used to distinguish between these two classes of enzymes.

E. S.

Further Experiments on the Isolation of the Antineuritic Vitamin. ATHERTON SEIDELL (*J. Amer. Chem. Soc.*, 1922, 44, 2042—2051; cf. Seidell, *J. Ind. Eng. Chem.*, 1921, 13, 1111).—The preparation of the vitamin solution is modified in that, instead of subjecting fresh yeast to autolysis and filtering the thick, slimy liquid thus obtained, the yeast is treated for a few minutes with boiling water and the mixture is then centrifuged. The aqueous solution thus obtained contains a greater proportion of the total vitamin than is present in the filtrate from autolysed yeast, and, in addition, is free from adenine and other products of the autolytic decomposition. The vitamin is adsorbed by fuller's earth from its acid solution (cf. Seidell, *U.S. Public Health Repts.*, 1922, 37, 801), thus giving an "activated solid" which is extracted with barium hydroxide solution and the barium eliminated by acidifying with sulphuric acid. The extract is subjected to precipitation with

saturated lead acetate solution and filtered. The filtrate is freed from excess of lead by means of hydrogen sulphide and concentrated by distillation under diminished pressure (the treatment with lead acetate prevents the otherwise excessive foaming during distillation). The residue is precipitated successively with silver nitrate and ammoniacal silver nitrate. Approximately one-third of the solids of the extract is precipitated as silver compounds, and these contain somewhat more than one-half of the antineuritic vitamin. The incomplete precipitation of the vitamin base is believed to be due to the considerable solubility of its silver compound.

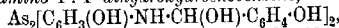
The vitamin fractions are found to be quite stable both in solution and in the dried condition. They dialyse almost completely through a collodion membrane and physiological tests show that all the vitamin is in the diffusate, thus indicating that the vitamin molecule is of relatively simple constitution. Using nitrogen estimations as a criterion of purity, it is concluded that the highly active fractions contain vitamin and one or more analogous nitrogenous bases, and that these cannot be advantageously separated from one another by silver precipitation. H. W.

Condensation Products of Arsphenamine [Salvarsan] with Aldehydes. GEORGE W. RAIZISS and A. C. BLATT (*J. Amer. Chem. Soc.*, 1922, **44**, 2023—2027).—A series of compounds of salvarsan with aldehydes of the general type,



has been prepared by dissolving 3:3'-diamino-4:4'-dihydroxy-arsenobenzene dihydrochloride in methyl alcohol, transformation of the latter into its di-sodium salt by the addition of four molecular proportions of aqueous sodium hydroxide and addition of slightly more than two molecular proportions of the requisite aldehyde. The mixture is in some cases agitated mechanically for two hours in an atmosphere of nitrogen, in others heated under a reflux condenser for a similar period. The product is precipitated by neutralising the solution with hydrochloric acid. The additive compounds are in general solids which vary in colour from yellow to reddish-brown. They cannot be crystallised readily from the customary organic media, and are in general merely washed and dried before being analysed.

The following individual substances are described: 3:3'-Bis-o- α -dihydroxybenzylamino-4:4'-dihydroxyarsenobenzene,



m. p. 182°, and the corresponding dihydrochloride, an orange-yellow substance. 3:3'-Bis- α -hydroxy-p-methoxybenzylamino-4:4'-dihydroxyarsenobenzene, a yellow powder which softens at 80° and decomposes gradually when further heated. 3:3'-Bis-p- α -dihydroxy-m-methoxybenzylamino-4:4'-dihydroxyarsenobenzene, from salvarsan and vanillin, a reddish-brown, amorphous solid, m. p. 175—176°. 3:3'-Bis-hydroxymethylamino-4:4'-dihydroxyarsenobenzene dihydrochloride, $\text{As}_2[\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{CH}_2(\text{OH})]_2\cdot 2\text{HCl}$, from salvarsan and formaldehyde, decomp. 185—190°. 3:3'-Bis- α -hydroxy-m-nitro-

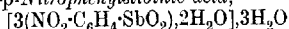
benzylamino-4 : 4'-dihydroxyarsenobenzene, a yellow powder, decomp. 247—250°. 3 : 3'-*Bis- α -hydroxy- γ -phenylallylamino-4 : 4'-dihydroxy-arsenobenzene*, $\text{As}_2[\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{CH}(\text{OH})\cdot\text{CH}:\text{CHPh}]_2$, from salvarsan and cinnamaldehyde, a yellow powder, decomp. 195—200°. Disodium salvarsan did not give products with benzaldehyde or *p*-chlorobenzaldehyde which were sufficiently pure for analysis.

H. W.

A Sulphonated Naphthylarsinic Acid. A. ELIZABETH HILL and A. K. BALLS (*J. Amer. Chem. Soc.*, 1922, **44**, 2051—2054).— α -Naphthylarsinic acid, creamy-white needles, m. p. 197°, is prepared conveniently by addition of a diazotised solution of α -naphthylamine to an aqueous solution of sodium arsenite and decomposition of the diazonium product at the atmospheric temperature. It is not affected by dilute or concentrated sulphuric acid, but is readily transformed by the fuming acid (20%) into a *monosulphonic acid*, colourless, somewhat hygroscopic, glistening plates, which remains unchanged below 250° (three *potassium* salts have been prepared). The substance is oxidised readily by alkaline potassium permanganate, but the viscous, yellow, hygroscopic liquid which is thereby obtained could not be purified; it is shown, however, to contain arsenic and sulphur in equal atomic proportion. The position of the sulphonic group in the naphthalene molecule has not been elucidated.

H. W.

***p*-Nitrophenylstibinic Acid.** G. CHARRIER (*Gazzetta*, 1922, **52**, ii, 16—18).—*p*-Nitrophenylstibinic acid,




(cf. Schmidt, A., 1920, i, 901), prepared by treating antimony trichloride with *p*-nitrophenyldiazonium chloride and subjecting the additive compound, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{SbCl}_4$, thus formed (cf. May, T., 1912, **101**, 1037), to the action of sodium hydroxide (cf. Bort, A., 1913, i, 115), forms an amorphous, chrome-yellow powder decomposing, without melting, at about 300°.


T. H. P.

Mercuriation in the Aromatic Series. II. Thymolmercuriacetates and their Derivatives. EFISIO MAMELI and ANNA MAMELI-MANNESSIER (*Gazzetta*, 1922, **52**, ii, 1—16; cf. this vol., i, 695).—By treating thymol with mercuric acetate under various conditions, the authors have obtained, besides the thymolmercuriacetate already known (cf. Dimroth, A., 1902, i, 850; Rupp, A., 1917, i, 670; Paolini, A., 1921, i, 902), also the two new compounds, thymol-2- and thymol-6-monomercuriacetates. The constitutions of these compounds are shown by the fact that they yield respectively an internal oxide and an ordinary oxide when treated in alkaline solution, which contains the corresponding hydroxides, with carbon dioxide. Confirmation of these structures is obtained by examining the behaviour of the compounds towards coupling with diazonium salts, Dimroth (*loc. cit.*) having shown that mercury groups in the ortho-position to a phenolic hydroxyl persist, whereas those in the para-position are often displaced by the azo-group. With thymol-6 mercuriacetate, not only is this

displacement observed, but a second azo-group enters in the ortho-position, the resulting compound being 2:6-bisbenzeneazothymol. The action of mercuric acetate on either thymol-2- or thymol-6-mercuriacetate yields thymoldimercuriacetate, which is the 2:6-compound.


Thymol-2-mercuriacetate,  $\text{Hg}\cdot\text{OAc}$, forms a lustrous,

crystalline, white powder, m. p. 147° on rapid heating, decomposing at 182° . It gives no coloration with ferric chloride, behaves towards sulphuric acid like its para-isomeride, and yields a black precipitate with ammonium sulphide in a few minutes and with hydrogren sulphide only when hydrochloric acid is present.


Thymol-6-mercuriacetate,  $\text{Hg}\cdot\text{OAc}$, forms small, lus-

trous crystals, m. p. 163° (bath initially at 150°), decomposing at 178 – 180° . It gives no coloration with ferric chloride, but dissolves in cold concentrated sulphuric acid, yielding a yellow coloration changing to reddish-brown. With benzenediazonium chloride, it gives (1) 2:6-bisbenzeneazothymol, m. p. 181° (cf. Mazzara and Pozzetto, A., 1885, 893; Auwers and Michaelis, A., 1914, i, 744), and (2) a small proportion of a cream-yellow azo-compound, which is possibly 2-benzeneazothymol-6-mercuriacetate.

Thymol-2-mercurichloride, $\text{OH}\cdot\text{C}_6\text{H}_4\text{MePr}\cdot\text{HgCl}$, has m. p. 144 – 145° , and decomposes at about 160° . The 6-isomeride crystallises in slender, white needles, m. p. 188° , and decomposes at 195° .

Thymol-2:6-dimercurichloride,  HgCl , has m. p. 210 –

211° (decomp.).

Thymol-2-mercuribromide forms a white, crystalline powder, contracting at 140° and reddening and subliming at 180° . The sulphate, $(\text{OH}\cdot\text{C}_6\text{H}_4\text{MePr}\cdot\text{Hg})_2\text{SO}_4$, is obtained as an amorphous, white powder, which reddens, without melting, at 220° . The nitrate forms a pale pink powder, turning violet in the light, m. p. 148 – 150° , decomposing at 155° . The oxide,  $\text{O}\cdot\text{Hg}$, forms a

white precipitate, m. p. 195° (decomp.), and has the normal molecular weight in freezing phenol.

Thymol-6-mercuribromide is a white compound, m. p. 149° (decomp.). The sulphate forms a white, amorphous powder, decomposing, without melting, at 235° , and dissolves in concentrated sulphuric acid to a yellow solution; careful addition of ferrous sulphate solution to this acid solution gives a wine-red ring or, on shaking, a greenish-blue coloration. The nitrate is a white, pulverulent substance with pale pink reflexion, m. p. 167° .

p p*

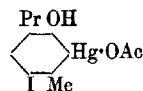
(decomp.), and dissolves in concentrated sulphuric acid to a straw-yellow solution which, with ferrous sulphate solution, gives a blood-red ring or, on agitation, a bluish-violet or intense blue

coloration. The oxide, $\left[\begin{array}{c} \text{Pr} \\ | \\ \text{OH} \text{---} \text{C}_6\text{H}_3 \text{---} \text{Hg} \text{---} \text{O} \\ | \\ \text{Me} \end{array} \right]_2$, forms a white

powder, blackens at 180° , decomposes into a gummy mass at about 205° , and exhibits normal cryoscopic behaviour in phenol solution. The hydroxide is a white compound, m. p. $190\text{--}195^\circ$ (decomp.).

T. H. P.

Mercuriation in the Aromatic Series. III. Mercuriated Derivatives of 6-Iodothymol. EFISIO MAMELI (*Gazzetta*, 1922, 52, ii, 18—23).—The action of mercuric acetate on 6-iodothymol, which has only one free ortho-position with respect to the hydroxyl, readily yields the monomercuri-derivative, 6-iodothymol-2-mercuri-



acetate (annexed formula), from which the corresponding chloride and bromide are obtainable. That the mercuri-group in all these compounds occupies the ortho-position with respect to the hydroxyl is shown by the formation of an internal oxide when the

iodothymolmercurihydroxide is treated with carbon dioxide. The action of iodine in presence of potassium iodide on 6-iodothymol-2-mercuriacetate yields a product identical with aristol; this result confirms the view that the iodine atom in aristol occupies the para-position with respect to the phenolic or quinonic oxygen and that the thymolic groups are united at the ortho-positions to this oxygen, these being the only free positions. Compounds showing the same behaviour as aristol are obtained also by the action of iodine and potassium iodide on thymol-2- and thymol-6-mercuriacetates (see preceding abstract).

6-Iodothymol-2-mercuriacetate forms white crystals, reddening at 170° , m. p. 175° (decomp.), yields 6-iodothymol when heated with concentrated hydrochloric acid, and gives with concentrated sulphuric acid a red coloration changing to green and later to brown. The corresponding chloride, $\text{OH} \cdot \text{C}_6\text{H}_3\text{MePrI} \cdot \text{HgCl}$, forms white crystals, turning yellow at 119° , m. p. $122\text{--}124^\circ$; the bromide is a white powder, turning yellow at 102° , m. p. $105\text{--}108^\circ$. The internal oxide, $\text{C}_6\text{HMePrI} \cdot \text{HgBr}$, forms crystals, m. p. $162\text{--}165^\circ$

(decomp.), and exhibits normal cryoscopic behaviour in phenol.

T. H. P.

Mercuriation in the Aromatic Series. IV. Dimercuriated Derivatives of Guaiacol. EFISIO MAMELI (*Gazzetta*, 1922, 52, ii, 23—27).—The action of mercuric acetate on guaiacol yields mono- and di-mercuriacetates in proportions varying with the experimental conditions; the principal product obtained in alcoholic acetic acid solution is guaiacol-4:6-dimercuriacetate. The positions of the two $\text{Hg} \cdot \text{OAc}$ groups are shown by the fact that the

action of nitric acid on this compound yields 4 : 6-dinitroguaiacol (cf. Cousin, A., 1900, i, 179).

With the dimercuriacetate and the corresponding dichloride and dinitrate, the acid residue united to the mercury is replaced with great readiness. For instance, replacement by hydroxyl is effected, not only by sodium hydroxide, but also by water or aqueous alcohol.

A dimercuri-derivative of 5-iodoacetylguaiacol has also been prepared and is being investigated.

Guaiacol-4 : 6-dimercuriacetate, $\text{OMe} \begin{array}{c} \text{OH Hg} \cdot \text{OAc} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_3 \\ \diagdown \quad \diagup \\ \text{Hg} \cdot \text{OAc} \end{array}$, forms white crystals, and turns yellow and then red, without melting, when heated; by concentrated sulphuric acid it is turned first green and then blue, and by water or aqueous alcohol it is converted into a white, infusible compound which is probably guaiacolmonomercuriacetate.

Guaiacol-4 : 6-dimercurihydroxide-3-oxide, $\text{OMe} \begin{array}{c} \text{OH Hg} \cdot \text{OAc} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_3 \\ \diagdown \quad \diagup \\ \text{O} \quad \text{Hg} \end{array}$, obtained by the action of 5% sodium hydroxide solution on the dimercuriacetate, forms an infusible, heavy, white precipitate and turns brown at 200—210°.

Guaiacol-4 : 6-dimercurichloride, $\text{OMe} \cdot \text{C}_6\text{H}_2(\text{OH})(\text{HgCl})_2$, forms a white, crystalline powder and begins to turn brown, without melting, at 179—180°; the nitrate, $\text{OMe} \cdot \text{C}_6\text{H}_2(\text{OH})(\text{HgNO}_3)_2$, is an infusible, white, crystalline compound. T. H. P.

Mercuriation in the Aromatic Series. V. Binary and Ternary Systems relating to Mercuriation. E. MAMELI and G. COCCONI (*Gazzetta*, 1922, 52, ii, 113—120; cf. preceding abstracts).—To explain the mechanism of mercuriation in derivatives of benzene, it has been suggested that the first phase of the reaction consists in the formation of an unstable intermediate compound either by substitution or addition. In order to ascertain if this is really the case in the mercuriation of phenol, the authors have investigated the freezing-point diagrams of the four systems, (1) $\text{Ph} \cdot \text{OH} - \text{Hg}(\text{OAc})_2$, (2) $\text{Ph} \cdot \text{OH} - \text{CH}_3 \cdot \text{CO}_2\text{H}$,

(3) $\text{CH}_3 \cdot \text{CO}_2\text{H} - \text{Hg}(\text{OAc})_2$, and (4) the ternary system. The diagram of state of system (1) exhibits a curve corresponding with the separation of phenol and ceasing at the concentration 50% at 17°; this curve indicates the formation of no product of combination. System (2) yields a complete curve which shows that the two components are miscible in the liquid condition and form no compound, and reveals a eutectic at 15.3°. For system (3), only the beginning of the curve corresponding with the separation of acetic acid is realisable. The ternary system is capable of development only for solutions rich in phenol, and is represented by a series of isothermal lines which indicate the formation of no additive product and come to an end

at the saturation curve of mercuric acetate in the phenol-acetic acid mixtures; this curve, separating the regions of saturated and unsaturated solutions, was confirmed by a series of measurements of solubility at 15°. No ternary eutectic point was observed. Further, the system aniline-mercuric acetate, within the limits of solubility of mercuric acetate in aniline, gives no indication of the formation of an additive product.

T. H. P.

Physiological Chemistry.

The Respiratory Exchange in Fresh-water Fish. III. Gold Fish. JOHN ADDYMAN GARDNER, GEORGE KING, and EDWIN BOOTH POWERS (*Biochem. J.*, 1922, **16**, 523-529).—Measurements were made with the apparatus previously described (*A.*, 1914, i, 1149). The consumption of oxygen was roughly proportional to the temperature. Gold-fish require much less oxygen per kilo. than trout, and appear to react to temperature over a wider range. The respiratory quotient showed unaccountable variations. E. S.

Relation between Age and the Concentrations of Protein Fractions in the Blood of the Calf and Cow. PAUL E. HOWE (*J. Biol. Chem.*, 1922, **53**, 479-494).—Estimations of the proteins in calves' blood from birth onwards indicate that the quantity and composition of the blood proteins are dependent on the diet during the first four to six weeks, but are afterwards independent of this factor. E. S.

Nature of the Reducing Substance in Human Blood. EVELYN ASHLEY COOPER and HILDA WALKER (*Biochem. J.*, 1922, **16**, 455-459).—The reducing power of blood is only occasionally increased by hydrolysis (cf. *A.*, 1921, i, 698). In the estimation of dextrose by MacLean's method, the presence of chlorides, bromides, iodides, or citrates inhibits the reduction of the copper carbonate; this action is not shown by sulphates or phosphates. Iodometric methods are not suitable for the estimation of blood sugar. Exercise frequently produces a considerable increase in the concentration of sugar in the blood. E. S.

Isolation of the Coagulating Enzyme from Blood-serum. MAX BLEIBTREU (*Pflüger's Archiv*, 1922, **194**, 318-322; from *Chem. Zentr.*, 1922, iii, 179).—A modification of an earlier method (Bleibtreu and Atzler, *A.*, 1920, i, 783). Serum casein is prepared by the addition of one gram of casein powder to 100 c.c. of ox-serum and precipitation by acetic acid. The precipitate after separation is reduced to a powder. Ten to 12.5 c.c. of 0.2-0.25 *N*-sodium hydroxide solution are added to 10 grams of serum casein in 50 c.c. of water. After addition of 100 c.c. of water

and neutralisation with *N*-hydrochloric acid, 15 c.c. of a diluted solution of "Liq. ferri oxyd. dialys.," 2.5 c.c. of saturated magnesium sulphate solution and half the volume of ethyl alcohol are added. The coagulating enzyme is obtained in the filtrate.

G. W. R.

Electrochemical Study of the Condition of Several Electrolytes in the Blood. B. S. NEUHAUSEN and E. K. MARSHALL, jun. (*J. Biol. Chem.*, 1922, 53, 365—372).—Electrometric methods have been used to estimate the concentrations of sodium, chlorine, and calcium ions in blood. The results indicate that sodium and chlorine are not bound to any appreciable extent, but are present as in an aqueous solution of sodium chloride and sodium hydrogen carbonate of the same concentration. About 80% of the calcium, however, is in the non-ionised form.

E. S.

The Action of the Phosphate-ion on Blood and Urinary Sugar. H. ELIAS and ST. WEISS (*Wiener Arch. inn. Med.*, 1922, 4, 29—58).—Intravenous injections of hypertonic solutions of sodium dihydrogen phosphate and sodium monohydrogen phosphate usually lower the sugar content of the blood in diabetic and alimentary hyperglycæmia, whilst the sugar content of normal blood is unaltered; the effect is accompanied and followed by a decreased excretion of sugar in the urine, and is due to the phosphate-ion. It cannot be ascribed to a decrease in the phosphorus content of the blood-serum, to the formation of dextrose diphosphoric acid or to oxidative glycolysis in the blood; the sugar must be removed either through some process of combustion or through the storing up of a carbohydrate or carbohydrate phosphoric acid in the tissues.

CHEMICAL ABSTRACTS.

Effect of Ether Anæsthesia on the Acid-base Balance of the Blood. DONALD D. VAN SLYKE, J. HAROLD AUSTIN, and GLENN E. CULLEN (*J. Biol. Chem.*, 1922, 53, 277—292).—During ether anæsthesia, the blood of dogs showed an increased hydrogen-ion concentration, a decreased alkaline reserve, and, with one exception, an increased carbon dioxide tension. A true acidosis thus occurs, due, apparently, either to the introduction of acid into the blood or the withdrawal of base from it. The latter change is not a secondary effect produced to balance an acapnia (cf. Henderson and Haggard, A., 1918, i, 201).

E. S.

Effects of Ether Anæsthesia alone or Preceded by Morphine on the Alkali Metabolism of the Dog. R. L. STEHLE, W. BOURNE, and H. G. BARBOUR (*J. Biol. Chem.*, 1922, 53, 341—348).—During ether anæsthesia the blood showed an increased hydrogen-ion concentration and a decreased alkali reserve. At the same time, the rate of excretion of sodium and potassium was lowered; this was probably due to the anuria which accompanies ether anæsthesia, for the total excretion of sodium and potassium during the day of the experiment was abnormally high. When administration of morphine preceded the ether anæsthesia, the increase in hydrogen-ion concentration was much less marked, whilst there

was practically no change in the alkali reserve. There was, however, a large increase in the rate of excretion of sodium and potassium.
E. S.

Erythropoietic Action of Germanium Dioxide. FREDERICK S. HAMMETT, JOSEPH E. NOWREY, jun., and JOHN H. MÜLLER (*J. Exptl. Med.*, 1922, **35**, 173—180).—Germanium dioxide causes a marked and sustained rise in the number of erythrocytes in blood which ranged from 1 to nearly 5 millions. The size of the dose did not seem to be important. The effect seems to be quick in making its appearance. The oxide also tends to increase the coagulability of the blood.
CHEMICAL ABSTRACTS.

Osmotic Resistance and Phosphatides of the Blood. New Quantitative Methods. R. BRINKMAN (*Arch. Néerland. Physiol.*, 1922, **6**, 451—515).—The author discusses in detail the various factors which affect the osmotic resistance of the red blood corpuscles. It is shown that whereas the resistance curves obtained when hypotonic solutions of sodium chloride are employed for estimating the osmotic resistance of the corpuscles show a gradual and continuous increase in hæmolysis with decreasing concentrations of salt, those obtained when equilibrated solutions containing physiological concentrations of calcium- and hydrogen-ions are employed consist of three distinct parts—a small fraction representing the old and least resistant corpuscles, a large fraction (80%) of somewhat greater resistance, and a small, strongly resistant fraction consisting of the young corpuscles. That continuous curves result when the former method is employed is due to an increased permeability of the cell which results from the lyotropic action of the sodium chloride on the lipoids which constitute the cell membrane. Pure solutions of sodium chloride are thus unsuitable for estimating the osmotic resistance of the cells. Solutions of a mixture of primary and secondary phosphates may, however, be employed. Details of the method are given, and it is shown that it gives results identical with those obtained with an equilibrated saline solution. The effect of changes in the organism of the ratio phosphatides: cholesterol has been studied and the hæmolytic action of phosphatides and its inhibition by cholesterol demonstrated (cf. A., 1920, i, 782).
E. S.

Uric Acid Content of Blood Corpuscles. A. CHAUFFARD, P. BRODIN, and A. GRIGAUT (*Compt. rend. Soc. Biol.*, 1922, **86**, 31—32; from *Chem. Zentr.*, 1922, i, 1209).—The uric acid content both of blood-serum and of blood corpuscles is twice as great in gouty conditions as in normal health. In the former case, the uric acid content of the corpuscles bears a more constant relationship to the uric acid content of the serum than in the latter case (cf. Theis and Benedict, this vol., i, 82).
G. W. R.

The Distribution of Chloride between Corpuscles and Plasma and the Influence of Carbon Dioxide. Z. DISCHER (*Biochem. Z.*, 1922, **131**, 594—600).—Contrary to the results of van Greveld (this vol., i, 287), there is no chloride in the corpuscles

of the circulating blood of normal persons or in the corpuscles of blood which has lost carbon dioxide through exposure. H. K.

Distribution of Sodium, Potassium, Calcium, and Magnesium between the Corpuscles and Serum of Human Blood. BENJAMIN KRAMER and FREDERICK F. TISDALL (*J. Biol. Chem.*, 1922, 53, 241—252).—Analytical results, to some extent collected from previous papers, are tabulated. E. S.

Soap and Serum. ADOLF JARISCH (*Klin. Woch.*, 1922, 1, 71).—Sodium soaps undergo hydrolysis in a medium having a p_H less than 8.5, but when soap is added to blood-serum, of which the p_H is far below this value, the liquid remains clear. To explain this fact, the author dialysed serum until it was free from salt and then added soap to one portion and colloidal fatty acid to the other. In each case a voluminous precipitate was obtained which had all the physical characteristics of euglobulin. This precipitate was completely soluble in a 0.012 *N*-solution of sodium chloride, which explains the fact that no precipitate is obtained with normal serum. Entirely similar precipitates are obtained when commercial lecithin or alcoholic extracts of tissue are added to dialysed serum. In every case, the precipitate soluble in sodium chloride solution appears to be an adsorption compound between the lipid and the pseudoglobulin of the serum. CHEMICAL ABSTRACTS.

Blood Enzymes. II. The Influence of Temperature on the Action of the Maltase of Dog's Serum. ARTHUR COMPTON (*Biochem. J.*, 1922, 16, 460—464).—The maltase present in dog's blood has an optimum temperature (55°) which shows no variation from animal to animal; this is probably due to the constancy of the hydrogen-ion concentration of the blood. The amount of this enzyme present, however, varies with different animals, although it remains practically constant for each individual. E. S.

Action of Nucleic Acid Injected into the Organism. Immunisation by a Single Injection. M. DOYON (*Arch. internat. physiol.*, 1921, 18, 307—312; *Ber. ges. Physiol.*, 11, 436; from *Chem. Zentr.*, 1922, i, 1206—1207; cf. this vol., i, 82).—Nucleic acid inhibits the coagulation of blood in vitro and in vivo, and increases the secretion of antithrombin similarly to peptone and other substances. A single injection in dogs confers immunity against the anticoagulating action of a second and third injection. Further effects of injection of nucleic acid are narcosis and lowering of blood pressure. An effective anticoagulating nucleoprotein (antithrombin) can be isolated from blood rendered incoagulable by nucleic acid. G. W. R.

The Action of Various Metallic Salts on Haemolysis. HELEN A. PURDY and L. E. WALBUM (*J. Immunol.*, 1922, 7, 35—45).—The significance of the presence of small quantities of metallic salts on the haemolytic action of saponin on horse blood corpuscles, of staphylolysin on goat blood corpuscles and of complement-amboceptor on sheep blood corpuscles was studied. By determin-

ing the minimal dose of the individual salts (in molar solution) at which their action is demonstrable, it is possible to obtain a comparison between the action of the different salts. Whilst some salts exert an inciting action on hæmolysis, others exert an inhibitive one (positive and negative catalysis?); some show an inciting effect at one concentration and an inhibitive one at another. The anion in the salts seems to be without significance as regards their action in either favouring or inhibiting hæmolysis.

CHEMICAL ABSTRACTS.

Hæmolysis by Morphine and Homologues. HEINRICH RHODE (*Biochem. Z.*, 1922, 131, 560—569).—Corpuscles washed with isotonic sodium chloride solution are hæmolysed by the hydrochlorides of morphine and its methyl, ethyl, and benzyl derivatives, the intensity of the action increasing in the order given. Bromides, sulphates, and phosphates of these alkaloids are weaker. Washing the corpuscles with sucrose solution instead of sodium chloride solution weakens the hæmolytic action of these alkaloids and reverses the relative hæmolytic activities of morphine, and methyl- and ethyl-morphine. A similar reversal is observed with ammonium salts.

H. K.

The Appearance of Digestive Enzymes during Fœtal Life. C. PORCHER and A. TAPERNOUX (*Compt. rend. Soc. Biol.*, 1920, 83, 619—620; *Expt. Sta. Record*, 44, 865).—The authors report the presence of trypsin, pancreatic amylase, pancreatic lipase, pepsin, and crepsin in the digestive tracts of three calf fœtuses aged seventy-five, one hundred, and one hundred and eighty days, respectively.

CHEMICAL ABSTRACTS.

The Influence of Illumination on the Metabolism of Carbohydrates. LUDWIG PINCUSSEN (*Klin. Woch.*, 1922, 1, 174).—A general illumination, following an injection of adrenaline, gives rise to an increase in the blood-sugar concentration. A decrease in the blood-sugar concentration is obtained if eosin is given previously to illumination. Adrenaline plus eosin plus light produces an effect that is the resultant of the two activities taken separately, the blood-sugar concentration being only slightly increased. The rate of oxidation of carbohydrates and allied substances is increased, in vivo, when the eosin-treated subject is illuminated. This is proved by the fact that when diabetics are so treated, the blood-sugar concentration decreases, the excretion of sugar into the urine decreases or disappears entirely and the acetone substances also largely disappear from the urine. Hypophyseal diabetics, with a large volume output of urine, are entirely refractory to illumination. The blood-sugar concentration is not changed by illumination with X-rays.

CHEMICAL ABSTRACTS.

Metabolism of Sulphur. V. Cysteine as an Intermediary Product in the Metabolism of Cystine. HOWARD B. LEWIS and DANIEL A. MCGINTY [with LUCIE E. ROOT] (*J. Biol. Chem.*, 1922, 53, 349—356).—Phenylcarbamidocysteine, when administered to rabbits, is excreted in the urine as phenylcarbamidocysteine.

Hence the first stage in the katabolism of cystine is probably conversion into cysteine (cf. this vol., i, 487).
E. S.

Considerations on the Solubility of the Phosphatides.
GUILLERMO V. STUCKERT (*Anal. Asoc. Quím. Argentina*, 1922, 10, 115—132).—The brains of oxen were fractionally extracted by various solvents. Not only are the solvent powers of different liquids mutually affected, but the solubility of constituents is affected by the order in which the material is treated by different solvents. The phosphatides and esterins cannot be separated in a state of purity by the use of neutral solvents. The lecithins obtained by fractional extraction are not chemically well-defined. Five distinct lecithin fractions are distinguished. Schemes are given showing the fractional separation of different constituents using acetone, ethyl alcohol, and ether.
G. W. R.

Chemistry of the Lungs. A New Phosphosulphatide.
UBALDO SAMMARTINO (*Biochem. Z.*, 1922, 131, 411—412; cf. A., 1922, i, 296).—From an alcoholic extract of the lipoids of the lungs a crystalline phosphosulphatide has been obtained containing phosphorus, sulphur, and nitrogen in the ratio 1 : 1 : 2. It has neither acid nor basic properties.
H. K.

Formation of Bilirubin in Surviving Spleen. Z. ERNST and B. SZAPPANYOS (*Klin. Woch.*, 1922, 1, 614—615; from *Chem. Zentr.*, 1922, i, 1118).—The spleen of dogs, surviving after death, forms bile pigments when irrigated with defibrinated blood containing dissolved hæmoglobin. The pigment formed resembles bilirubin and the amount formed is about seven times the amount formed by the liver during the same period.
G. W. R.

Alkaligenesis. II. Ammonia Production in Muscle.
OLIVE P. LEE and S. TASHIRO (*Amer. J. Physiol.*, 1922, 61, 244—253; from *Physiol. Abstr.*, 1922, 7, 344).—1 Gram of resting frog's gastrocnemius gives off 3.83×10^{-7} grams of ammonia in fifteen minutes. During 360 contractions, it produced 7.56×10^{-7} grams. Tetanised and injured muscle produces none owing to the simultaneous production of volatile acid. Ammonia held by tetanised muscle is released on recovery: in injured muscle it is not. Muscle gives off 1/14 as much as nerve.
W. O. K.

The Degradation of Carbohydrates in Transversely Striated Muscles. II. FRITZ LAQUER (*Z. Physiol. Chem.*, 1922, 122, 26—45; cf. this vol., i, 298).—The rate of disappearance of glycogen and of formation of lactic acid by frog muscle has been further studied with special reference to the season of the year. It has also been observed that glycogen is converted into lactic acid more readily than dextrose, and that destruction of the cell structure by repeated freezing in liquid air results in an inability to produce lactic acid from dextrose whilst there is no decreased production from glycogen. This suggests that an intermediate precursor of lactic acid is a more reactive form of dextrose, which is produced directly in the case of glycogen.
W. O. K.

Creatinine and Creatine in Muscle Extracts. III. Concerning the Presence of Enzymes in Muscle Tissue which have Creatine and Creatinine as their Substrates. FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1922, 53, 323—337; cf. A., 1921, i, 907).—The conversion of creatine into creatinine proceeds three to four times more rapidly in muscle extract than in aqueous solution. That this is not due to the presence of an enzyme in muscle extract is shown by the fact that there is no diminution in the rate in extracts which have been boiled, and only a slight diminution in those which have been centrifuged. Moreover, the amount of creatinine formed in a given time in a dialysed extract is only slightly greater than that produced, under the same conditions, in an equal volume of the dialysate (the initial concentrations of creatine and creatinine are the same, owing to the ease with which these substances dialyse). The increased rate of conversion of creatine into creatinine is apparently due to the colloids present in muscle extract. These adsorb creatinine but not creatine. Further, their state of aggregation undergoes periodic changes, corresponding with which periodic changes in the rate of formation of creatinine occur. The reaction is thus catalysed by the "milieu" provided by living tissue. Such types of catalysis are called biocatalysts in contradistinction to those which require the addition of a foreign catalyst. In its later stages, the reaction $\text{creatine} \rightarrow \text{creatinine}$ in muscle extract is a reaction of the first order. E. S.

Cell Penetration by Acids. VI. The Chloroacetic Acids. W. J. CROZIER (*J. Gen. Physiol.*, 1922, 5, 65—79).—The rate of penetration of the tissue of *Chromodoris zebra* by acid varies with the concentration and strength of the acid, and also with the temperature. From measurements, it is concluded that the rate of penetration is controlled chiefly by the rate of diffusion, but that chemical factors also enter in. W. O. K.

Classification of Aromatic Odours in Sub-classes. 8. OHMA (*Arch. Néerland. Physiol.*, 1922, 6, 567—590).—From numerous fatigue experiments the author concludes that the aromatic class in Linné's classification of odours must continue to form one class. Three sub-classes may, however, be distinguished, namely, the odour of benzaldehyde, the odour of camphor, and the odour of citral. The members of these sub-classes, together with transition members, are indicated. E. S.

Analysis of Camel's Colostrum. HELEN L. FALES (*J. Biol. Chem.*, 1922, 53, 339).—The following results were obtained: fat 7.4, sugar 4.2, casein 4.1, albumin 0.5, globulins, etc., 0.8, ash 0.893, CaO 0.272, MgO 0.025, P₂O₅ 0.318, K₂O 0.164, Na₂O 0.082, Cl 0.128%. E. S.

Phosphate Excretion in the Urine during Water Diuresis and Purine Diuresis. JOHANNES BOCK and POUL IVERSEN (*K. Danske Videnskab. Selskab. Biol. Medd.*, 1921, 3, 1—28).—In water diuresis of rabbits, there is no connexion between the amount of phosphate excreted and the volume of the urine. Profuse theo-

phylline diuresis is accompanied by an increase in the phosphate content of the urine, but appears not to be connected therewith; the phosphate content of the plasma is practically unchanged or reduced after administration of theophylline. Thus the augmented excretion of phosphate in the urine is not dependent either on an increased concentration of phosphate in the plasma or on the volume of the urine, but must be attributed to a specific action of theophylline on secretory elements of the kidney, probably other than those producing the diuresis.

CHEMICAL ABSTRACTS.

The Action of Intravenous Injections of Dextrose and Gum Arabic Solution on Diuresis. KARL CORI (*Wiener klin. Woch.*, 1921, **34**, 169—171).—Hypertonic dextrose solution administered intravenously has a strong diuretic effect on dogs, similar to molar diuresis. Abundant excretion of chloride-ion results, accompanied by a correspondingly large quantity of water. On diets containing only a small amount of chlorine, less chlorine is excreted and diuresis is also diminished. After twenty-four hours the increased flow of chlorine into the blood from the tissues can still be observed. The absorption and excretion of nitrates administered by mouth were accelerated by the effect of dextrose, as shown by Stejskal. In man, dextrose solution has no diuretic effect, as the chlorine adheres more closely to the tissues. Seven per cent. gum arabic solution injected intravenously reduces the sugar excretion of the diabetic. Simultaneously, the amount of urine decreases. In dogs, gum arabic solution causes a diminished excretion of ingested iodine as compared with control animals. The gum solution proves of weak diuretic effect in experiments on dogs and there is no increased excretion of chlorine. It is therefore a question of water diuresis as opposed to dextrose diuresis.

CHEMICAL ABSTRACTS.

The Rôle of Hexamethylenetetramine in the Production of Hæmaturia. W. A. BLOEDORN and J. E. HOUGHTON (*J. Lab. Clin. Med.*, 1922, **7**, 514—533).—A high hydrogen-ion concentration of urine favours the elimination of formaldehyde thereby and appears to be a necessary factor in the production of hæmaturia following administration of hexamethylenetetramine; in most cases, administration of suitable quantities of sodium hydrogen carbonate will prevent the liberation of formaldehyde. If hexamethylenetetramine is dependent for its antiseptic properties on the liberation of formaldehyde, these properties can never be manifested except in the genito-urinary tract.

CHEMICAL ABSTRACTS.

The Nature of Ehrlich's Diazo-reaction. III. LEO HERMANN (*Z. physiol. chem.*, 1922, **122**, 93—103; cf. A., 1921, i, 531).—After coupling with dichlorobenzendiazonium chloride, a substance, $C_{14}H_9O_4N_2Cl_2$, dark red, irregular prisms, m. p. 68—70°, has been isolated from the urine of tuberculous patients. This indicates that the substance originally present, responsible for the diazo-reaction, has the formula $C_8H_6O_4$. It has phenolic properties.

A different substance appears to be responsible for the diazo-reaction in cases of typhus, but enough could not be isolated for analysis.

Dichlorobenzenediazonium chloride couples with benzylhistidine to yield a *bisdiazobenzoylhistidine*, $C_{25}H_{15}O_3N_3Cl_2$, a red dye, but this is not analogous to that obtained from urine. W. O. K.

Adrenaline Hyperglycæmia. BRÖSAMLEN (*Deut. Arch. klin. Med.*, 1921, **137**, 299—310; *Ber. ges. Physiol.*, **11**, 510; from *Chem. Zentr.*, 1922, i, 1252).—Subcutaneous injection of 1 mg. of adrenaline induces an increase in blood sugar of about 0.058% in healthy individuals. The hyperglycæmia begins after ten minutes, reaches a maximum after one hour, and passes after two to three hours into a slight hypoglycæmia. In diabetes mellitus, adrenaline hyperglycæmia shows no simple behaviour. The adrenaline blood-sugar curve may possibly be separable into a pancreatogenous and a neurogenous form. G. W. R.

Unsaturated Alcohols obtained from the Fat of Ovarial-dermoid Cysts. JOHANN MUCK (*Z. physiol. chem.*, 1922, **122**, 125—142).—Neither cholesterol nor ischolesterol is present in the fat of ovarian-dermoid cysts. An alcohol present, related to cholestol and giving similar colour reactions, yields a bromo-derivative, $C_{11}H_{20}OBr_2$, a white, sandy powder, m. p. 150° (decomp.). On boiling with alcoholic potassium hydroxide solution, the bromine is removed and a substance formed giving the colour reactions of a cholestol compound.

By reducing the mixed alcohols, no definite results have been obtained, but from the products of oxidation there has been isolated an amorphous monobasic acid, $C_{19}H_{34}O_4$, apparently formed from the cholestol compound (calcium salt, $C_{38}H_{66}O_8Ca \cdot 2H_2O$; barium salt, $C_{38}H_{66}O_8Ba \cdot 2H_2O$; silver salt, $C_{19}H_{33}O_4Ag$). W. O. K.

Amino-acid Deficiency Probably the Primary Etiological Factor in Pellagra. JOSEPH GOLDBERGER and W. F. TANNER (*U. S. Public Health Rep.*, 1922, **37**, 462—486).—Details are given of the occurrence of pellagra in a number of individuals who were known to be receiving diets containing adequate supplies of mineral elements and of the known vitamins. By eliminating these factors, the author concludes that pellagra is caused by a deficiency in the diet of some special combination or combinations of amino-acids. A large amount of literature leading to the same conclusion is quoted. Administration of cystine alone and of a mixture of cystine and tryptophan appears to produce some improvement in the disease. E. S.

Chlorine Metabolism in Pulmonary Tuberculosis. FELIX BOENHEIM (*Beitr. Klin. Tuberk.*, 1921, **49**, 233—238).—There appears to be a parallel between the severity of pulmonary tuberculosis and hypochloræmia; a diminished gastric chlorine secretion is not universal, so that the chlorine of the blood cannot be the decisive factor in gastric secretion. Since in the majority of cases gastric secretion is diminished early, the increased chlorine in the

blood is excreted by the kidneys, resulting in a condition of hypochloræmia, whilst normal or increased gastric secretion is associated with irritability of the gastric cells, the blood chlorine not utilised by the gastric glands being eliminated by the kidneys. Alternatively, the hypochloræmia may be due to anchoring of the chlorine in tissue depots. There is experimental evidence that in tuberculosis there is a dechlorination and resulting chlorine starvation of the tissues.

CHEMICAL ABSTRACTS.

Pharmacological Examination of isoPropyl Alcohol. D. I. MACHT (*Arch. int. pharmacodynamie*, 1922, 26, 285—286).—isoPropyl alcohol is more toxic than ethyl alcohol or methyl alcohol, and less toxic than n-propyl alcohol. Administration by the mouth produces narcosis, in larger doses general anæsthesia, and finally coma and death. Very little is absorbed by inhalation, and there is very little evidence of its absorption through the skin.

CHEMICAL ABSTRACTS.

Mode of Oxidation of Fatty Acids with Branched Chains. II. **The Fate in the Body of Hydratropic, Tropic, Atrolactic, and Atropic Acids together with Phenylacetaldehyde.** HERBERT DAVENPORT KAY and HENRY STANLEY RAPER (*Biochem. J.*, 1922, 16, 465—474).—The substances were administered to dogs. Tropic and atrolactic acids were not appreciably attacked. Hydratropic and atropic acids, however, were both oxidised, the former partly (66%) and the latter completely. The unchanged hydratropic acid recovered from the urine contained the *d*-form in excess. It is concluded that the first stage in the oxidation of hydratropic acid is its conversion into atropic acid. This is probably further oxidised to formylphenylacetic acid (cf. A., 1914, i, 1122), which is then completely destroyed. Dakin's observation that phenylacetaldehyde is to a large extent oxidised in the body has been confirmed.

E. S.

Fate of some of the Phenylacetylated Amino-acids in the Animal Organism. GEORGE J. SHIPLE and CARL P. SHERWIN (*J. Biol. Chem.*, 1922, 53, 463—478).—The phenylacetyl group is apparently as effective as the benzoyl group in protecting amino-acids from oxidation in the animal organism. Thus, the phenylacetyl derivatives of glycine, alanine, leucine, glutamic acid, glutamine, aspartic acid, and ornithine are excreted unchanged in the urine after administration to man, dogs, rabbits, and chickens (cf. this vol., i, 492; Thierfelder and Sherwin, A., 1915, i, 481, 750).

Phenylacetyl-dl-alanine, feathery clusters, m. p. 150—152°, was prepared by the action of phenylacetyl chloride on alanine. Phenylacetyl-dl-leucine, feathery clusters, m. p. 133—134°, was similarly prepared from leucine.

E. S.

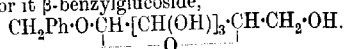
[Physiological] Effect of Cyanamide. ERICH HESSE (*Z. Ges. exp. Med.*, 1922, 26, 337—351; from *Chem. Zentr.*, 1922, i, 1150).—Observations on the effect of cyanamide, previously administered, in modifying the physiological action of certain substances.

G. W. R.

The Action of the Digestive Juices on β -Benzyl-*d*-glucoside. A. RICHAUD (*Compt. rend. soc. biol.*, 1922, 86, 770—772).—The author incubated the macerated mucous membrane of the dog with β -benzyl-*d*-glucoside in the presence of two preservatives (toluene and sodium fluoride), but could not find any measurable trace of sugar split off even after thirty-six hours. It is therefore concluded that the substance is not attacked by the emulsin of the intestinal tract and is absorbed into the circulation unchanged.

CHEMICAL ABSTRACTS.

The Toxicity of β -Benzylglucoside obtained by Biochemical Synthesis. A. RICHAUD (*Compt. rend. Soc. Biol.*, 1922, 86, 649—651).—The author attempted to overcome the relative toxicity of benzyl benzoate introduced by Macht as an antispasmodic by substituting for it β -benzylglucoside,



This has the advantage over benzyl benzoate in that it is more soluble in water and is less irritating to the tissues. Administered subcutaneously, the toxic dose for the mouse or guinea-pig is 11—12 grams per kilo. For the rabbit the toxic intravenous dose is 8—9 grams per kilo.

CHEMICAL ABSTRACTS.

Chemistry of Vegetable Physiology and Agriculture.

The Growth-promoting Factor of Lemon Juice. BRUNO LEICHTENTRITT and MARGARETE ZIELASKOWSKI (*Biochem. Z.*, 1922, 131, 499—512).—The growth-promoting factor of lemon juice, for bacteria, has been submitted to a variety of experimental conditions. Lemon juice heated at 100° in acid or alkaline solution is practically unaltered in its growth-promoting factor for bacteria. Even hydrolysis with 2% hydrochloric acid is without influence, although sodium hydroxide is inimical. Exposure to ultra-violet light in Rontgen rays is without action whatever the reaction of the medium, and aeration in boiling solution is also without action. Adsorbents weaken the action but incompletely, and the bacterial growth-promoting principle is dialysable independently of the reaction of the medium.

H. K.

Growth-promoting Factor of Lemon Juice. BRUNO LEICHTENTRITT and MARGARETE ZIELASKOWSKI (*Biochem. Z.*, 1922, 131, 513—524).—There is little parallelism between the effect of external conditions and reagents on the bacterial growth-promoting principle and the antiscorbutic factor *C* of lemon juice as tested on guinea-pigs and children. Lemon juice contains an antiscorbutic factor *C* and a factor which promotes growth of bacteria and of ill-nourished children. This latter factor is termed factor or vitamin-*D*. Further experiments are necessary to determine whether *D* is identical with vitamin-*B* or not.

H. K.

The Presence of Nucleic Acid in Bacteria. A. J. SCHAFER, CASPAR FOLKOFF, and S. BAYNE JONES (*Bull. Johns Hopkins Hosp.*, 1922, **33**, 151).—A nucleic acid, containing guanine and phosphorus, half of which is easily split off and half firmly bound, but no pentose, was obtained from *Bacillus coli*.

CHEMICAL ABSTRACTS.

The Elective Action of Tellurium Salts on Bacteria of the Colon-typhoid Group. G. JOACHIMOGLU (*Z. Urol.*, 1922, **16**, 97—100).—Telluric acid in concentrations of 1 in 40,000 has an elective inhibitive action on the growth of *Bacillus coli* and *B. typhosus* in cultures. It is suggested that this substance be used in colon bacillus infections of the urinary tract.

CHEMICAL ABSTRACTS.

The Darkening of Carbohydrate containing Nutrient Media by *Bacillus mesentericus* var. *niger*. ANNA MUSCHEL (*Biochem. Z.*, 1922, **131**, 570—590).—*Bacillus mesentericus* var. *niger* grows on agar devoid of carbohydrates, multivalent alcohols, or amino-acids which are not derivatives of benzene without coloration of the medium, but in presence of sugars, alcohols, and tyrosine with darkening of the media. By use of protein-free media, it is shown that the coloration is due to benzene derivatives related to *o*- and *p*-dihydroxybenzenes with possible condensation with amino-acids.

H. K.

Production of Hydrogen Peroxide by Bacteria. JAMES WALTER McLEOD and JOHN GORDON (*Biochem. J.*, 1922, **16**, 499—506).—The substance inhibitory to its own growth produced by the *Pneumococcus* in the presence of an abundant supply of oxygen (cf. *Lancet*, 1921, i, 900; *J. Path. Bact.*, 1922, **25**, 139) is hydrogen peroxide. When grown on a medium of agar and heated blood ("chocolate agar") a green coloration is produced. This is due to the action of the hydrogen peroxide which is formed; a similar action is shown by certain streptococci which also produce hydrogen peroxide. Stimulation of the growth of the *Pneumococcus* by fresh tissue fluids is probably due to the presence in the latter of catalase.

E. S.

Chemical Problems in the Bacteriology of Tubercle Bacillus. ESMOND R. LONG (*Amer. rev. tubercul.*, 1921, **5**, 705—714; *Ber. ges. Physiol.*, **12**, 299; from *Chem. Zentr.*, 1922, iii, 173).—Experiments with different strains of acid stable bacteria showed that alanine, leucine, and histidine can each serve as able source of nitrogen supply. Tryptophan and phenylalanine are not utilised, possibly on account of the toxic character of their decomposition products. The synthesis of carbohydrate is not effected simply with the carbon of amino-acids; a further source of carbon is necessary, preferably glycerol. Propionamide and ammonia are utilised by all bacteria studied. Creatinine is only utilised by certain saprophytes. Urea is not attacked by tubercle bacilli, frog bacilli, or fish bacilli.

G. W. R.

Influence of Hydrogen-ion [Concentration] on the Growth of *Azotobacter*. P. L. GAINNEY and H. W. BATCHELOR (*Science*, 1922, 56, 49—50).—The maximum hydrogen-ion concentration permitting the growth of *Azotobacter* isolated from different soils is p_H 5.9—6.0. It was found that as the hydrogen-ion concentration of the soil decreased, growth increased until p_H 6.1—6.4 was reached. The optimum reaction for the fixation of nitrogen appears to be very closely associated with that for growth. The total quantity of acid produced by the various cultures was insignificant.

A. A. E.

The Decomposition of Kaolin by Organisms. W. J. VERNADSKY (*Compt. rend.*, 1922, 175, 450—452).—Experiments carried out to determine whether formation of hydrated aluminium oxide occurs by the action of diatoms on naturally occurring aluminium silicates showed that silicious diatoms developed in a medium in which the only source of silica was clay, whilst no action took place in the sterilised control experiment. In the former case, the clay was found to contain free aluminium hydroxide, but none was detected in the control. The author suggests that this decomposition may play a considerable part in natural processes.

H. J. E.

Nitrification. KOJI MIYAKE and S. SOMA (*J. Biochem. [Japan]*, 1922, 1, 123—129).—Nitrification as a whole is an auto-catalytic unimolecular chemical reaction and increase of nitric acid is in accordance with the expression: $\log x - \log (A - x) = K(t - t_1)$. The decrease of ammonia compounds in the soil is also an auto-catalytic reaction following the expression: $\log (A - x) / \log (x - a) = (A - a)Kt - K_1$, where x = ammoniacal nitrogen at the end of time t , and A and a denote the original and final amounts of ammonia. K and K_1 are constants.

CHEMICAL ABSTRACTS.

Urea as a Nutrient of Yeasts and other Plants. TH. BOKORNY (*Allgem. Brauer. Hopfenztg.*, 1922, 243—246; from *Chem. Zentr.*, 1922, i, 1146; cf. A., 1917, i, 680).—In a comparison of urea and hippuric acid, it is shown that the former is an ideal plant nutrient both on account of its high nitrogen content and also because it liberates carbon dioxide. Hippuric acid is less satisfactory, since it gives benzoic acid and glycine, both of which are poisonous or harmful to plant life.

G. W. R.

Lactic Acid Fermentation of Dextrose by Peptone. GOTTFRIED SCHLATTER (*Biochem. Z.*, 1922, 131, 362—381).—Dextrose is converted quantitatively by peptone at 37° into inactive lactic acid, sodium hydrogen carbonate being used as buffer. This buffer substance may be replaced by sodium acetate, but not by phosphate mixtures, owing to flocculation of the peptone. During the fermentation, amino-acids appear and fermentation ceases, with flocculation of the peptone. Peptones free from phosphates, as, for example, Witte's peptone, give no fermentation; most of the observations recorded were made on Siegfried peptone. The solu-

tions are not quite sterile, although no known lactic acid forming bacteria were found.

H. K.

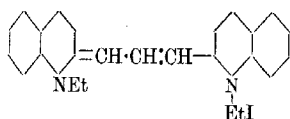
Peptone Fermentation. EMIL BAUR and EUGEN HERZFELD (*Biochem. Z.*, 1922, **131**, 382—385).—The authors draw an analogy between the glycolytic action of plant and animal juices and the fermentation of dextrose by peptone, as revealed by their own experiments or by those of Schlatter (previous abstract). Schlatter's observations are considered an effective reply to Bau's criticism (this vol., i, 307) of their own experiments in fermentation without yeast (this vol., i, 93).

H. K.

The Oligodynamic Effect of Silver. IV. R. DOERR and W. BERGER (*Biochem. Z.*, 1922, **131**, 351—361).—The active agent in all oligodynamic effects is the silver ion. Silver surfaces lose their activity by treatment with potassium cyanide, and water activated by silver is inactivated by potassium cyanide. The inactivation is due to conversion of the deleterious silver ion into $\text{Ag}(\text{CN})_2$ ions. Carbon dioxide and oxygen are each more potent than air in developing the oligodynamic action of silver surfaces.

H. K.

The Antiseptic Properties of Cyanine Dyes. C. H. BROWN-ING, J. B. COHEN, and R. GULBRANSEN (*Brit. Med. J.*, 1922, I, 514—515; cf. this vol., i, 612).—Certain of the cyanine dyes are extremely potent antiseptics, for example, sensitol red (annexed formula)



for staphylococci in aqueous medium. Selective antiseptic action as between staphylococcus and *Bacillus coli* is exhibited to a higher degree by sensitol-red (for example) than by any other com-

compound hitherto investigated, the ratios of the sterilising concentrations probably being greater than 2000:1. Sensitol-green is the most active of these dyes both in serum and aqueous medium for *B. coli*. Also, in the case of *B. coli*, the antiseptic action in serum is more intense than in aqueous medium.

A. A. E.

Energy Changes accompanying the Assimilation of Carbon Dioxide. O. WARBURG and ERWIN NEGELEIN (*Z. physikal. Chem.*, 1922, **102**, 235—266).—Experiments are described in which the green alga, *Chlorella vulgaris*, has been subjected, in a suitable environment, to the light from a metal filament lamp, and the proportion of the absorbed energy converted into chemical energy deduced by measuring the volume of oxygen liberated. This change occurs according to the equation $6\text{CO}_2 + 6\text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 - 674000 \text{ cal.}$ Further measurements have been made to ascertain the proportion of the chemical energy which is converted into heat.

J. F. S.

Adsorption of Nutrients and Plant Growth in Relation to Hydrogen-ion Concentration. ÓLOF ARRHENIUS (*J. Gen. Physiol.*, 1922, **5**, 81—88).—The rates of growth and of germin-

ation and of the adsorption of salts vary with the P_H of the nutrient medium. The variation is particularly marked in regard to absorption. The greatest absorption of anions occurs when the reaction is acid.

W. O. K.

Phosphorus Nutrition of Plants. M. VON WRANGELL (*Landw. Jahrb.*, 1922, 57, 1—78; from *Chem. Zentr.*, 1922, i, 1387).—From a large number of pot-culture experiments with different plants it is concluded that the power of any species to utilise the phosphorus of relatively insoluble mineral phosphates varies directly with the ratio $\text{CaO} : \text{P}_2\text{O}_5$ in its ash. In the following series, in which the $\text{CaO} : \text{P}_2\text{O}_5$ ratio is given in brackets, phosphorus utilisation is shown in increasing degree:—wheat and rye (1·3), barley and oats (1·6), maize (3), beans, peas, and vetches (about 7), clovers (12), rape (23), tobacco, hemp, and mustard (15), buckwheat (17). Acid soil reaction favours anion absorption, whilst alkaline reaction favours cation absorption and the composition of the plant is thereby affected. Thus oats grown with acid soil reaction gave a ratio $\text{CaO} : \text{P}_2\text{O}_5$, 0·6; with neutral soil reaction, 10·0. The depressing effect of calcium ions on phosphorus absorption is postponed in the case of plants showing high calcium absorption. Where the absorption of phosphoric oxide from a fertiliser is greater than that of calcium oxide, the growth of a crop results in an excess of calcium oxide in the soil which may be undesirable. G. W. R.

Plant Chemistry. IV. *Juncus effusus*, L. JULIUS ZELLNER (*Monatsh.*, 1922, 43, 120—123).—A record of certain analytical data for this plant.

C. K. I.

Estimation and Distribution of Chlorine in Plants. J. JUNG (*Sitzungsber. Akad. Wiss. Wien*, 1920, 129, 297—340).—By the use of either (a) 0·5 gram of thallium acetate and 2 grams of glycerol in 7·5 grams of water, or (b) 0·1 gram of silver nitrate in 9·9 grams of 10% ammonia solution, chlorine was detected microchemically in numerous plants; it is absent from only a few plants, notably the conifers. It occurs only as chloride, and usually increases in amount from the roots to the leaves, being most abundant in succulent, parenchymatous tissues, apparently dissolved in the cell sap. It is usually scarce in the epidermis, bundles, hairs, flower parts, pollen, woody tissue, and chlorophyllous mesophyll, and abundant in fleshy roots and rhizomes. Plants which grow in rich, moist soil and in the sea are richer in chlorine than those growing in sandy soil, heaths, and fresh water. Mosses, ferns, epiphytes, parasites, and saprophytes contain little or no chlorine.

CHEMICAL ABSTRACTS.

Relation between Manganese Content and Proportion of Ash in Young and Old Leaves. F. JADIN and A. ASTREUC (*Bull. Soc. chim.*, 1922, 31, 917—921).—A study of the comparative manganese content of young and old leaves leads to the conclusion that the figures obtained on analysis should be regarded as having only a relative value. The quantity of manganese in relation to the fresh material is less in the case of young leaves, and for the

dry material a similar result is obtained although the variations are not so great. In relation to the ash, however, the variations are in the inverse sense, although several exceptions are noted. The authors discuss the bearing of their results on those obtained by Bertrand and Rosenblatt (A., 1921, i, 759). H. J. E.

The Occurrence of Cobalt and Nickel in Plants. GABRIEL BERTRAND and M. MOKRAGNATZ (*Compt. rend.*, 1922, 175, 458—460).—The authors have developed their method of detecting and estimating traces of cobalt and nickel, and now describe its application to the examination of the following vegetables: carrot, onion, potato, spinach, lettuce, cress, tomato, apricots, beans, lentils, buckwheat, wheat, oats, maize, rice, mushroom. Nickel was found in the ash in each case, and, with the exception of carrot and oats, cobalt also. It is pointed out that these two negative results may be reversed in working with larger quantities of ash. The proportion present is minute: that of cobalt varies from less than 0.005 mg. to 0.3 mg. per kilo. of the fresh substance, whilst in the case of nickel the values range from 0.01 mg. to 2.0 mg. H. J. E.

Anthochlor. G. KLEIN (*Sitzungsber. Akad. Wiss. Wien*, 1920, 129, 341—394).—The yellow pigment from 300 species of flowers was examined; of these, 60 contained anthochlor, the rest mostly carotin. Its occasional simultaneous occurrence with carotin, flavone, and anthocyanin was proved, and its close relation to anthocyanin in the case of closely related plants was established. It is not a single pigment, but a group of closely related ones. It is a glucoside. Its reactions with concentrated mineral acids, alkalis, metallic salts, and reducing agents are discussed.

CHEMICAL ABSTRACTS.

Synthesis of Vitamin-A by a Marine Diatom (*Nitzschia closterium*, W. Sm.) Growing in Pure Culture. HENRY LISTER JAMESON, JACK CECIL DRUMMOND, and KATHARINE HOPE COWARD (*Biochem. J.*, 1922, 16, 482—485).—The marine diatom, *Nitzschia closterium*, is able to synthesise large amounts of vitamin-A when grown in Miquel's solution or in sterilised sea water.

E. S.

The Constituents of the Flowering Tops of *Artemisia* *fra*, Jacq. JOHN AUGUSTUS GOODSON (*Biochem. J.*, 1922, 16, 489—493).—The following substances have been isolated: camphor, a wax-like ester which was probably ceryl cerotate, tricontane, copoletin, and quebrachitol. The camphor had $[\alpha]_D^{25} + 9.7^\circ$ and was evidently a mixture of the two enantiomorphs. No compounds were found which could be regarded as related to santonin.

E. S.

Chemical Composition of Belladonna Leaves. A. GORIS and A. LARSONNEAU (*Bull. Sci. Pharmacol.*, 1921, 28, 499—503; from *Chem. Zentr.*, 1922, i, 757).—Belladonna leaves are extracted with (dilute) sulphuric acid. After addition of excess of soda, the ethereal extract yields, on crystallisation, at first hyoscyamine,

mixed later with a little atropine. From the residue of the ethereal extract a volatile oil is obtained which has an odour like that of pyridine and contains pyridine, 1-methylpyrrolidine, and 1-methylpyrrolidine. The aqueous extract yields an unidentified 1:4-diamine of pleasant, tobacco-like odour.

G. W. R.

Oils and Fats from the Seeds of Indian Forest Trees. MADYAR GOPAL RAU and JOHN LIONEL SIMONSEN (*Indian Forest Records*, 1922, 9, Part III).—The seeds of *Chloroxylon Swietenia* yield 16% of a non-drying oil consisting of glycerides of stearic, palmitic, myristic, oleic, and linolenic acids. The seeds of *Calophyllum wightianum* yield 34% of an oil closely resembling that obtained from the seeds of *C. inophyllum* and containing about 10% of resin and glycerides of stearic, palmitic, oleic, and linolic acids. The seeds of *Mimusops elengi* yielded 16% of oil consisting of glycerides of stearic, palmitic, and oleic acids, and an unidentified saturated acid which was possibly behenic acid. The seeds of *Shorea robusta* yield 16.4% of a fat resembling Borneo tallow and consisting of glycerides of stearic and oleic acids. *Garcinia cambogia* seeds yield 31% of a fat resembling the fats from other species of *Garcinia* which should prove an excellent edible fat. It consists of glycerides of stearic and oleic acids.

H. C. R.

Sand Spur, *Cenchrus tribuloides*, L. HEBER W. YOUNGKEY and CHARLES H. LA WALL (*Amer. J. Pharm.*, 1922, 94, 567—583).—The mature fruits of the sand spur, *Cenchrus tribuloides*, L., give the following results. Moisture, 8.17%; ash, 3.95% (containing silica 10%); water-soluble extractives, 3.55% (including 0.55% of reducing sugars, the remainder being of mucilaginous character); alcoholic extractives, 3.17%, mainly chlorophyll, and resinous and oily constituents; light petroleum extractives, 2%, principally fat; ethyl ether extractives, 3.3%, having acid number 19.10, saponification number 197, and iodine number 60. Alkaloids, glucosides, and toxic or irritating substances were absent.

G. W. R.

Stearic Acid in the Latex of *Ficus fulva*, Reinw. A. J. ULTÉE (*Bull. Jard. bot. Buitenzorg*, 1922, [iii], 5, 105—106).—The latex contains large quantities of a wax, which on hydrolysis yields stearic acid. There is but little rubber present. *Ficus elastica* latex contains much smaller quantities of a different wax.

G. B.

Fluorine in Spanish Grapes. MARTINIANO LEGUIGAMÓN PONDAL (*Anal. Asoc. Quím. Argentina*, 1922, 10, 57—73).—Fluorine is found to be a normal constituent in Spanish grapes. A method is described for its detection, using the etching action of hydrogen fluoride on glass.

G. W. R.

The Influence of Light on the Formation of Anthocyanin in the Scales of Lily Bulbs (*Lilium candidum* and *L. Martagon*). MARCEL MIRANDE (*Compt. rend.*, 1922, 175, 496—498).—The curve of pigmentation has been traced by the use of mono-

chromatic filters, and shows a maximum in the red, a minimum in the green, and a more important maximum in the indigo-blue region. Rays in the non-luminous portion of the spectrum have no action.

H. J. E.

The Changes and Movements of the Saccharine Materials in *Mercuriale vivace* (*Mercurialis perennis*, L.) in the Course of its Annual Growth. P. GILLOT (*J. Pharm. Chim.*, 1922, vii], 26, 250—258).—The content of reducing sugars in the aerial portions of the plant does not vary greatly from season to season. In the subterranean parts, the reducing sugar is greatest in quantity in the young growing portions. In the older organs, rhizomes, etc., it attains its maximum in the summer and a minimum at the beginning of the spring. The polysaccharides in the aerial parts of the plant appear to consist almost entirely of sucrose, and the same applies to the underground shoots. The rhizomes and roots give extracts which remain dextrorotatory even after hydrolysis by invertase, and the presence of a dextrorotatory substance in addition to sucrose is therefore postulated. The proportions of this dextrorotatory substance appear to vary with the season, existing only in small quantity at the time of inflorescence. It increases in quantity to a maximum in August. Considerable quantities of sucrose were isolated from the rhizome juices, but attempts to isolate the dextrorotatory principle have been up to the present unsuccessful.

G. F. M.

Proteins of the Lima Bean, *Phaseolus lunatus*. D. B. JONES, C. E. F. GERSDORFF, C. O. JOHNS, and A. J. FINKS (*J. Biol. Chem.*, 1922, 53, 231—240).—The lima bean contains 21.17% of protein ($N \times 6.25$). By extraction with sodium chloride solution, an α - and a β -globulin were obtained which were separated by fractional precipitation with ammonium sulphate. An albumin was also isolated. Analyses by Van Slyke's method gave the following values for basic amino-acids: α -globulin—cystine 1.60, arginine 0.67, histidine 3.71, lysine 7.84%; β -globulin—cystine 0.84, arginine 0.07, histidine 2.62, lysine 8.53%; albumin—cystine 1.07, arginine 0.74, histidine 2.54, lysine 5.97%. Positive tests were obtained for tryptophan in each case. The proteins of the lima bean are, in general, similar to those of other beans of the genus *Phaseolus* (cf. this vol., i, 504).

E. S.

Swedish Pines and Spruces. H. E. WAHLBERG (*Svensk Pappers-Tidning*, 1922; *Papierfabr.*, 1922, 20, 1097—1100, 1133—137, 1178—1181).—The test-stems were cut up systematically and sample disks taken from definite points, these disks being further subdivided into numbered sectors. Estimations of moisture, apparent specific gravity, ash, resin, and cellulose were made in order to establish any regular variations in different portions of the tree. The most variable function is the apparent specific gravity; generally the wood having the narrowest annual rings had the highest density. The ratio of the apparent specific gravity of the autumn wood to that of the spring wood had an average value

of 1.92 throughout the tree, in spite of considerable variations in the absolute values for the different annual rings. Comparing the weather records for various years with the corresponding annual rings, it appeared that a wet, cold season tended to give rise to wood of low density. The apparent specific gravities of the freshly felled wood and of the seasoned wood were compared; shrinkages of 6.5 to 11.6% in volume were recorded during the transition from the growing tree to the air-dry condition. Cellulose and resin tended to vary inversely but generally without regular laws; the principal variation in this respect was a tendency for the cellulose to decrease and the resin to increase from the outer layers towards the heart. The resin appears to have reached a constant condition of solubility within ten days after felling [cf. *J. Soc. Chem. Ind.*, 1922, 805A].

J. F. B.

The Chemical Constituents of Green Plants. XX. The Acids of the Cherry (*Prunus avium*). HARTWIG FRANZEN and FRITZ HELWERT (*Z. physiol. chem.*, 1922, 122, 46—85).—Malic acid is much the most important acid of the cherry. There are present also traces of oxalic acid, and small quantities of succinic acid, citric acid, lactic acid, and of unsaturated acids.

W. O. K.

Mafulra Tallow, a Product of the Nuts of *Trichilia emetica*. M. RINDL (*South African J. Ind.*, 1922, 5, 415—423).—Both the husk and the kernel of Mafulra nuts from Portuguese East Africa furnish a solid fat, whilst an oil is obtained from the aril. The aril oil has the following characters: d_{40}^{25} 0.931, acid value (as oleic acid) 8.9%, saponification value 202.5, iodine value 66, saponification value of acetylated oil 235. The oil congeals if kept for some time at about 5°. The constants of the solid fat obtained from different sources vary so widely that it is certain that all the commercial material is not derived from the same species of *Trichilia*. The kernel usually contains about 60% of fat, and the husk 25—35%. It has a high m. p., ranging usually from 35—45°, and yields 7—8% of its weight of glycerol on saponification. It has a notably high acid value (40—50).

G. F. M.

The Phytin Content of Foods. E. ARBENZ (*Mitt. Lebensm. Hyg.*, 1922, 13, 45—52).—Finely pulverised foods (vegetables and fruits dried first at 36°) were extracted with 0.6% hydrochloric acid, the phytin being estimated in the extracts by an adaptation of the method of Huebner and Stadler (*Biochem. Z.*, 1914, 64, 422). The percentages of phytin (as anhydrous phytic acid) in fresh and dried fruits, respectively, were: Rice bran, 3.801, 4.232; rice flour, 0.192, 0.216; wheat bran, 4.641, 5.073; whole-wheat flour, 0.498, 0.572; white flour, 0.184, 0.208; maize flour, 0.764, 0.857; lentils, 0.292, 0.326; peas, 0.498, 0.561; oat flour, 0.460, 0.506; cocoa, 2.110, 2.230. Phytin was not found in carrots, turnips, cauliflower, Brussels sprouts, kale, spinach, asparagus, apples, peaches, or figs.

CHEMICAL ABSTRACTS.

Effect of Silicic Acid on Crop Production in the Presence of Insufficient Amounts of Phosphoric Acid. O. LEWERMANN and H. WIESSMANN (*Z. Pflanz. Düng.*, [A], 1922, 1, 185—255).—Working with sand cultures of gramineous, leguminous, and cruciferous plants, increases in yield were obtained by the use of colloidal silicic acid, particularly in the presence of insufficient phosphoric acid. In experiments with natural soils, similar results were obtained. With shortage of nitrogen or potassium, the effect of silicon is much less. The increases appear to be due to the direct action of silicic acid on plant growth. Silicon compounds, other than colloidal silicic acid, gave insignificant or negative results.

G. W. R.

The Growth of Maize as Affected by Iron and Aluminium Salts. CHAS. H. ARNDT (*Amer. J. Bot.*, 1922, 9, 47—71).—The availability of iron in ferric phosphate depends largely on the composition of the nutrient solution, the requisite quantity of ferric phosphate varying from 7 mg. per litre in one case to more than 35 mg. in another. 0.0005*N*-Ferrous sulphate gave optimum growth in one case and the addition of ferric nitrate produced a precipitate from which the plant could not obtain sufficient iron from a 0.001*N*-solution. Sulphuric, nitric, and hydrochloric acids are approximately equal in toxicity when added to the nutrient solutions in low concentrations; at higher concentrations, sulphuric acid depressed the growth of tops more than the others, but was more favourable to root development. Sand cultures required much more acid than water cultures to produce the same results. The toxicity of ferrous sulphate showed no relation to the initial hydrogen-ion concentration. Aluminium salts produced approximately the same depression in growth as a solution of ferrous sulphate of the same normality.

CHEMICAL ABSTRACTS.

Characteristic Proteins in High- and Low-protein Maize. M. F. SHOWALTER and R. H. CARR (*J. Amer. Chem. Soc.*, 1922, 44, 2019—2023).—The relative abundance of the different proteins in maize and the contents of mono- and di-amino-acids have been studied.

A considerably larger part of the protein is present as zein and globulins in high-nitrogen than in low-nitrogen maize; the zein and globulins have been formed at the expense of the amides, albumin, and gluten. The embryo constitutes about 15% of the total weight of high nitrogen maize grain, whereas dent maize of the usual composition has only about 11% of embryo. Zein appears to be the protein which is present in most variable amount, averaging 50.28% in high-nitrogen and only 31.85% in low-nitrogen maize. The protein of high-nitrogen "popcorn" is particularly rich in zein, averaging 57.24%. The total nitrogen content appears to determine the amounts of the various proteins.

The amino-nitrogen in the filtrate from the bases is found to be higher in the high-nitrogen maize than in that of low nitrogen content. The di-amino acids constitute approximately twice as

great a percentage of the total nitrogen in high-nitrogen as in low-nitrogen maize.

H. W.

Water-soluble Constituents of the Alfalfa Plant (Lucerne). THOMAS B. OSBORNE, ALFRED J. WAKEMAN, and CHARLES S. LEAVENWORTH (*J. Biol. Chem.*, 1922, **53**, 411—429).—The investigation of the press-juice previously obtained (this vol., i, 99) has been continued. After removal of the colloid obtained by addition of 20% of alcohol, a second precipitate may be obtained by raising the alcohol content of the filtrate to 53%. This precipitate contains 8% of the original nitrogen, which is probably present as protein. The distribution of nitrogen, both before and after hydrolysis, has been determined in the two precipitates and also in the filtrate, and analyses have been made of the inorganic constituents of the three fractions. The filtrate appears to be suitable for investigating the water-soluble constituents of the juice; the present paper records preliminary experiments in this direction.

E. S.

Comber's Reaction for Acidity of Soils. J. HUDIG and C. W. G. HETTERSCHIJ (*Chem. Weekblad*, 1922, **19**, 366—367).—The colour given by the reagent, an alcoholic solution of potassium thiocyanate, cannot be taken as a quantitative indication of acidity for sandy humus-bearing soils, since it does not indicate the same order as the hydrogen-ion determination. As Comber has pointed out, quantitative results are precluded, although for the same soil the test may indicate variations in acidity.

S. I. L.

Soil Reaction and Succession in Relation to Plant Covering. E. J. SALISBURY (*Ann. Bot.*, 1922, **36**, 391—431).—An account of the soils of the dune, shingle, and salt marsh system of Blakeney Point (Norfolk). In the successive stages of dune formation the content of calcium carbonate diminishes owing to leaching, whilst the content of organic matter increases. Hydrogen-ion concentration shows a corresponding variation, the reaction of the older dunes being more acid than that of the younger dunes. A close relationship exists between organic matter and water content. Shingle banks show similar relationships. In salt marshes, however, tidal effects obscure other factors.

G. W. R.

Influence of Soil Colloids on Availability of Salts. NEIL E. GORDON and E. B. STARKEY (*Soil Sci.*, 1922, **14**, 1—7).—Iron oxide and alumina gels have considerable adsorptive power for calcium acid phosphates, but the adsorption by silica gel is small. Within limits, adsorption increases with increasing concentration of the salt solutions. Adsorbed salts are only slowly released from the gel in contact with water. The hydrogen-ion concentration of the salt solution considerably affects the amount adsorbed. With silica gel the adsorption of calcium and potassium decreases, and of phosphate slightly increases, with decreasing p_H values. A. G. P.

Organic Chemistry.

The Action of Ozone on Hydrocarbons with Special Reference to the Production of Formaldehyde. I. The Action of Ozone on Methane. T. SHERLOCK WHEELER and E. W. BLAIR (*J. Soc. Chem. Ind.*, 1922, **41**, 331—332t).—Mixtures of methane and ozonised oxygen in proportions outside the explosive limits of 4% and 60% of methane were passed, with and without admixture with ammonia, through a tube which could be heated to any desired temperature in an electric furnace, at such a rate that the gas was heated for about two and a half minutes. At 15°, the reaction is very slow; it increases with the temperature until, at 100°, 53% of the ozone reacts in about two minutes, and 76% at 200°. Above 400° all the ozone decomposes. The first isolated product was formaldehyde, which is quickly further oxidised, but initially the oxidation rate does not increase so fast as that of methane and there is a slight increase in the amount isolated up to about 300°. The amount was not increased when ammonia was present, but the amount of formic acid isolated was much increased in these circumstances owing to formation of ammonium formate. In absence of ammonia only traces of formic acid remained unoxidised, and the greater portion of the methane oxidised was obtained as carbon dioxide and water formed from formic acid either by way of carbonic acid or by its decomposition into carbon dioxide and hydrogen, the latter being then oxidised to water. The non-stabilisation of formaldehyde by the ammonia is ascribed to the necessity of ten molecules interacting to form hexamethylenetetramine, which does not readily occur at such low concentrations. G. F. M.

The Absorption of Ethylene by Sulphuric Acid. Preparation of Ethyl Alcohol, Ethyl Sulphate, and Liquid Hydrocarbons. A. DAMIENS (*Compt. rend.*, 1922, **175**, 585—588; cf. A., 1913, ii, 349).—The effect of a catalyst on the speed of fixation of ethylene by sulphuric acid is considerable; cuprous oxide, which is transformed by the acid into cuprous sulphate, is the most efficient among the substances used. Whatever the nature of the final product may be, the reaction in the presence of the catalyst takes place in two stages: (1) the formation of a complex, $\text{Cu}_2\text{SO}_4 \cdot n\text{C}_2\text{H}_4$, partly soluble in sulphuric acid, (2) the action of the acid on this complex. The latter may yield either ethyl hydrogen sulphate and diethyl sulphate, or liquid hydrocarbons. The formation of the ethyl compounds occurs in the cold; the equilibrium $\text{H}_2\text{SO}_4 + \text{Et}_2\text{SO}_4 \rightleftharpoons 2\text{HETSO}_4$ is displaced from left to right by elevation of temperature and by hydration of the acid. Formation of a mixture of saturated hydrocarbons of density 0.77 and b. p. 110° and upwards takes place when the catalyst is heated in contact with the acid, followed by absorption of the

gas at the ordinary temperature in presence of mercury or mercurous sulphate.

H. J. E.

Reactions of Combination with Conjugated Systems of Double Linkings. I. Bromination of Isoprene. A. G. BERGMANN (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 24—37).—Molecules composed of two similar atoms or groups of atoms unite with a conjugated system of double carbon linkings at the 1- and 4-positions, that is, at the ends of the system, an exception to this rule occurring in the combination of bromine with aromatic derivatives. As regards molecules consisting of dissimilar components, such as hydrogen bromide, few experimental data are available, but the union does not take place in accordance with Thiele's law.

Bromination of isoprene in chloroform solution cooled in ice yields: (1) A small quantity of the monobromo-compound, $\text{CH}_3\text{Br}\cdot\text{CMe}:\text{C}:\text{CH}_2$ (?), b. p. $61.5\text{--}62.5^\circ/64\text{ mm.}$, d_4^{20} 1.3742. (2) The dibromide, $\text{C}_5\text{H}_8\text{Br}_2$, b. p. $62\text{--}64^\circ/10\text{ mm.}$, d_4^{20} 1.7431, which gives the dibromo-glycol, b. p. 126.5° , when oxidised by permanganate. (3) The isomeric dibromide, b. p. $88\text{--}92^\circ/10\text{ mm.}$, d_4^{20} 1.7880. This dibromide yields a viscous, oily ozonide, which is decomposed by boiling water, giving bromoacetone, bromoacetic acid, and a tarry mixture of bromoaldehydes, bromoketones, peroxides, etc. Oxidation of the dibromide by means of permanganate yields the dibromo-glycol, which is sparingly soluble in water, whilst treatment with chromic acid gives bromoacetone and bromoacetic acid (cf. Mokiewsky, A., 1899, i, 726; 1900, i, 509; *J. Russ. Phys. Chem. Soc.*, 1904, 36, 912). With ammonia, the dibromide forms an amorphous, sometimes glue-like substance of high molecular weight, and with sodamide an amorphous, insoluble product containing 32.51—32.89% of bromine and 7.87—7.93% of nitrogen.

T. H. P.

Reactions of Combination with Conjugated Systems of Double Linkings. II. Combination of Hydrogen Bromide with Diisopropenyl [$\beta\gamma$ -Dimethyl- $\Delta^{\alpha\gamma}$ -butadiene]. A. G. BERGMANN (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 37—40).—The combination of hydrogen bromide with $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene in glacial acetic acid solution takes place in the two stages: (1) $\text{CH}_3\cdot\text{CMe}:\text{CMe}:\text{CH}_2 + \text{HBr} = \text{CMe}_2\text{Br}\cdot\text{CMe}:\text{CH}_2$, and (2) the latter $+ \text{HBr} = \text{CMe}_2\text{Br}\cdot\text{CMe}_2\text{Br}$ (30%) $+ \text{CMe}_2\text{Br}\cdot\text{CHMe}\cdot\text{CH}_2\text{Br}$ (70%). γ -Bromo- $\beta\gamma$ -dimethyl- Δ^{α} -butene, $\text{C}_6\text{H}_{11}\text{Br}$, b. p. $84\text{--}86^\circ/100\text{ mm.}$, d_4^{20} 1.2201, yields dimethylisopropenylcarbinol when hydrolysed by means of aqueous potassium hydroxide.

$\beta\gamma$ -Dibromo- $\beta\gamma$ -dimethylbutane was described by Thiele (A., 1894, i, 217).

$\alpha\gamma$ -Dibromo- $\beta\gamma$ -dimethylbutane is a liquid, b. p. $88\text{--}89^\circ/16.5\text{ mm.}$, d_4^{20} 1.6065.

The product of the union of 1 mol. of hydrogen bromide with isoprene, namely, γ -bromo- γ -methyl- Δ^{α} -butene, combines with a second molecule of hydrogen bromide, apparently giving only $\beta\beta$ -dibromo- β -methylbutane.

T. H. P.

Formation of Acetylene and Ammonia during Incomplete Combustion. K. A. HOFMANN and ERICH WILL (*Ber.*, 1922, 55, [B], 3228–3233).—The gaseous products of an inverted air flame burning in the vapours of several organic substances have been investigated. The necessary apparatus is fully figured and described in the original text. The supply of air is so adjusted that the flame just burns continuously. The following quantities of acetylene (in grams) are obtained by the decomposition of 100 grams of the organic compound: benzene, 5; phenol, 4.4; aniline, 2.5; diphenylamine, 2.7; carbazole, 2.4; pyridine, 1.7; anthracene, 1.6; anthracene residues, 0.24; coal tar, 4; middle-oil from Rositzer lignite tar, 1; benzoquinone, 1; hexane, 2. The formation of acetylene is partly due to thermal action, but oxidative degradation also plays a part, as is proved by the production of the gas from hexane. Hydrocyanic acid is also present in the gases (100 grams of aniline, carbazole, diphenylamine, and pyridine yield, respectively, up to 3, 1.5, and 5 grams and traces of hydrocyanic acid).

The possibility of the production of ammonia during the combustion of air charged with a number of catalysts in hydrogen or coal gas has also been investigated. The actual quantity formed is very small, but the effect of the catalyst is clearly perceptible. Arsenic trihydride, chromyl chloride, and silicon tetrachloride depress the formation of ammonia. Osmium tetroxide and the osmium formed therefrom and, in particular, nickel carbonyl are active catalysts. The action of the latter, by which metallic nickel is produced, appears to indicate that the effect is due to a catalytic hydrogenation of the nitrogen, and not to an influence of the flame ions. The carbon liberated from benzene vapour or coal gas favours the production of ammonia, possibly owing to intermediate formation of hydrogen cyanide. The yields of ammonia are not improved noticeably by bringing volatile salts, such as sodium or lithium carbonates, into the flame, by spreading the flame over a porous clay surface impregnated with various salts or by placing an inverted mantle over the orifice of the burner.

H. W.

Calcium Carbide. ERLING BOTOLFSSEN (*Ann. Chim.*, 1922, 18, 5–48).—Pure calcium carbide is not obtained by heating calcium acetylide-acetylene-ammonia, $C_2Ca, C_2H_2, 4NH_3$ (cf. Moissan, A., 1899, i, 241; 1903, i, 545), as this substance, even when pure, yields an impure product containing free carbon, cyanamide, calcium cyanide, and probably calcium nitride and hydride. A diagrammatic representation of this decomposition is given, but it is pointed out that the series of reactions is more complex than the diagram indicates. A study of calcium-ammonia shows that its formation may take place at temperatures ranging from -15° to $+30^\circ$ (cf. Moissan, A., 1899, ii, 152); at the higher temperature, pressure is required, and, if the calcium employed contains sodium as impurity, the product is pasty rather than crystalline. On being heated under reduced pressure, the substance decomposes

explosively; the temperature at which this occurs depends on the pressure. The author considers that the calcium-ammonium hitherto described is a mixture. The reaction between metallic calcium and free carbon is not appreciable at temperatures below the melting point of the metal. Above 800°, combination takes place more rapidly if the calcium is in the state of vapour. When the carbide is prepared in an iron tube, the product, even when practically pure, is black, the coloration being due, not to free carbon, but to iron, and on substituting alundum for iron a similar coloration is caused by aluminium which has been reduced by calcium. On heating calcium carbide, dissociation into its elements was observed without any intermediate formation of a sub-carbide. The progress of the dissociation is influenced by the presence of iron, iron oxide, and other substances.

H. J. E.

The Oxidation of *iso*Propyl Alcohol with Potassium Permanganate. WILLIAM LLOYD EVANS and LILY BELL SEFTON (*J. Amer. Chem. Soc.*, 1922, 44, 2271—2276; cf. A., 1912, i, 743; 1916, i, 362; 1919, i, 514).—When oxidised by potassium permanganate in the presence of potassium hydroxide, *isopropyl* alcohol yields carbon dioxide, oxalic acid, and acetic acid. In addition, a small amount of acetone is obtained if the temperature does not exceed 25° and the concentration of the alkali does not exceed 2.12 grams per litre. The amounts of oxalic and acetic acids produced increase and decrease respectively as the initial alkalinity increases from zero to 0.1—0.2 *N*. The general effect of temperature is to increase the amount of carbon oxidised to carbon dioxide to slightly more than one atom for each molecule of alcohol.

Oxalic acid is obtained in greater quantity from *isopropyl* alcohol in neutral solutions than from acetone, owing to the fact that in the first step of the reaction no acids are formed to neutralise the potassium hydroxide obtained from the potassium permanganate. Further, the course of the oxidation is such as to bring about a final concentration of alkali which is greater than in the oxidation of acetone alone.

W. G.

A Simplified Method for the Resolution of Methyl-*n*-hexyl-carbinol. JOSEPH KENYON (*T.*, 1922, 121, 2540—2542).

Synthetic Experiments with Ethenylcarbinols. I. Conversion of γ -Methyl- Δ^4 -butinen- γ -ol into γ -Methyl- Δ^4 -butinene, β -Methylbutanolone, and its Condensation Products. HELMUT SCHEIBLER and ARTUR FISCHER (*Ber.*, 1922, 55, [B], 2903—2923).—The preparation of γ -methylbutinenol, $\text{OH}\cdot\text{CMe}_2\cdot\text{C}\equiv\text{CH}$, and its conversion into *isopropenyl*acetylene, $\text{CH}_2\cdot\text{CMe}\cdot\text{C}\equiv\text{CH}$, has been described by Farbenfabriken vorm. F. Bayer & Co. in a series of patents (cf. A., 1916, i, 113, 305). The preparation of the pure alcohol on a laboratory scale, and the applications of it for synthetic purposes are now described.

Finely divided sodamide is placed beneath ether which is cooled by ice and saturated with acetylene which has been purified by

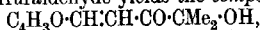
means of bleaching powder, copper nitrate solution acidified with nitric acid, concentrated sulphuric acid, and soda-lime. When saturation is complete, the subsequent current of acetylene is caused to pass through acetone heated at 30–40°, so that the sodium acetone as it is formed reacts immediately with the gas. The product thus obtained consists of a mixture of γ -methylbutinenol, mesityl oxide, and β -dimethyl- Δ^7 -hexenene-3 α -diol, $\text{OH}\cdot\text{CMe}_2\cdot\text{C}\equiv\text{C}\cdot\text{CMe}_2\cdot\text{OH}$, m. p. 94°. Since γ -methylbutinenol and mesityl oxide can only be separated from one another incompletely by fractional distillation, the carbinol is purified by conversion into its silver derivative and subsequent decomposition of the latter by the theoretically necessary quantity of dilute hydrochloric acid. γ -Methylbutinenol, b. p. 103–104°, is a colourless, mobile liquid, with a characteristic odour, which mixes with water in all proportions and strongly reduces alkaline permanganate solution. It has d_4^{25} 0.8651, n_D^{25} 1.41867, d_4^{15} 0.8678, n_D^{15} 1.41536, n_D^{18} 1.42446. With mercuric chloride, it gives a compound, decomp. above 240° without melting below 300°. Its copper and potassium derivatives are described. It is converted by acetic anhydride and sodium acetate into the corresponding acetate, a colourless liquid, b. p. 128–136°, which could not be obtained in a state of purity.

The conversion of γ -methylbutinenol into isopropenylacetylene by anhydrous magnesium sulphate at 250° is described in detail, and sketches are given of the necessary apparatus. The yields of the hydrocarbon are 15–18% of those theoretically possible; the unusual volatility of the product renders its complete condensation a matter of great difficulty. When freshly distilled, it is a colourless, mobile liquid with a very penetrating odour; it has b. p. 32–35°, d_4^{15} 0.6801, n_D^{15} 1.41666, n_D^{11} 1.43046. It gives a white precipitate with ammoniacal silver nitrate solution, and a highly characteristic, lemon-yellow cuprous derivative.

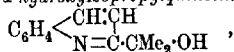
An ethereal solution of magnesium ethyl bromide reacts with isopropyleneacetylene (in the same manner as with acetylene) to yield ethane and magnesium isopropyleneacetylenyl bromide; the latter is converted by isobutyraldehyde into the secondary alcohol, $\text{CH}_3\cdot\text{CMe}_2\cdot\text{C}\equiv\text{C}\cdot\text{CH}(\text{OH})\cdot\text{CHMe}_2$, but the product is not homogeneous, and when reduced by sodium and moist ether gives a mixture of substances, b. p. 75–90°/15 mm., and 110–125°/15 mm., respectively.

The mode of the addition of the elements of water to γ -methylbutinenol varies considerably with the catalyst employed. It is converted by dilute sulphuric acid in the presence of mercuric sulphate into a voluminous, white precipitate which disappears after a few minutes with formation of β -methylbutane- β -ol- γ -one (methyl α -hydroxyisopropyl ketone), $\text{OH}\cdot\text{CMe}_2\cdot\text{COMe}$, b. p. 140–141°, $d_4^{17.2}$ 0.9578, n_D 1.41425, n_D 1.42203 (semicarbazone, m. p. 164°; oxime, m. p. 86°; acetate, a colourless liquid with an odour resembling peppermint, b. p. 171–172°, $d_4^{17.4}$ 1.0064, $n_D^{17.4}$ 1.41485, $n_D^{17.4}$ 1.42302). It condenses with benzaldehyde in aqueous alcoholic solution in the presence of sodium hydroxide to form α -phenyl-

δ -methyl- Δ^2 -pentene- δ -ol- γ -one (benzylidenemethyl α -hydroxyisopropyl ketone), $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{OH}$, a greenish-yellow, very highly refractive liquid, b. p. 164–169°/15 mm., m. p. 39–40° (oxime, m. p. 136°; acetate, m. p. 85°). α -3:4-Methylenedioxyphenyl- δ -methyl- Δ^2 -pentene- δ -ol- γ -one (piperonylidenemethyl α -hydroxyisopropyl ketone) is prepared from β -methylbutanolone and piperonal, crystallises in lustrous, yellow leaflets, m. p. 105–106°; the corresponding acetate forms coarse, yellow crystals, m. p. 93°. α -Phenyl- ζ -methyl- Δ^2 -heptadiene- ζ -ol- ϵ -one (cinnamylidenemethyl α -hydroxyisopropyl ketone), pale yellow leaflets, m. p. 109–110°, and its acetate, almost colourless crystals, m. p. 58–59°, are described. In a similar manner, furfuraldehyde yields the compound,



a pale yellow, highly refractive, viscous liquid which rapidly darkens on exposure to air, b. p. 140–145°/15 mm. (acetate, colourless, lustrous leaflets, m. p. 49°). β -Methylbutanolone and *o*-aminobenzaldehyde yield 2- α -hydroxyisopropylquinoline,



a colourless, crystalline powder, m. p. 64–65°.

In the absence of mercury salts, γ -methylbutinenol is transformed by boiling dilute sulphuric acid into isopropenylacetylene and probably also methyl isopropenyl ketone, $\text{CH}_2\cdot\text{CMe}\cdot\text{COMe}$, whereas β -methylbutanolone is not produced. A solution of sulphuric acid in glacial acetic acid also converts γ -methylbutinenol into isopropenylacetylene and, ultimately, into an undistillable resinous condensation compound.

β -Methylbutan- β -ol- γ -one is converted by phosphoric oxide in the presence of light petroleum at the atmospheric temperature into a substance, $\text{C}_{10}\text{H}_{18}\text{O}_5$, a colourless liquid with an odour resembling camphor, b. p. 163–167°, d_4^{20} 0.9702, n_D^{20} 1.41696, n_D^{25} 1.42456. It is stable towards permanganate, does not yield an oxime or semicarbazone, and does not react with acetic anhydride. Its physical constants point to the presence of three oxygen atoms in ether-like combination as indicated by the formula $\text{O}\left(\text{CMe}\begin{smallmatrix} \text{CMe}_2 \\ \text{O} \end{smallmatrix}\right)_2$.

Such a compound must have the properties of an acetal. This is found to be the case, since it is hydrolysed by concentrated hydrochloric acid to β -methylbutanolone, and is transformed by bromine into a dibromo-compound (?), $\text{O}\left(\text{C}(\text{CH}_2\text{Br})\begin{smallmatrix} \text{CMe}_2 \\ \text{O} \end{smallmatrix}\right)_2$, a colourless, crystalline powder, m. p. 64–65°. H. W.

The Action of Boric Acid on Mannitol in Alkaline Solution. RENÉ DUBRISAY (*Compt. rend.*, 1922, 175, 762–764; cf. A., 1918, ii, 368; this vol., ii, 428).—The addition of increasing quantities of mannitol to a solution containing boric acid and sodium hydroxide, in the proportions of 1/10 mol. of each substance per litre, results in increase of the minimum temperature at which complete miscibility of the solution with phenol occurs. Measurement of the rotatory power of such solutions shows that it increases until the

molecular ratio of mannitol to boric acid is 1.2 to 1, and thence decreases with increase of the ratio. Similar results are obtained with a solution in which the concentrations of boric acid and sodium hydroxide are doubled. A series of observations on the surface tension of the two solutions is also recorded.

H. J. E.

Derivatives of Behenic and Erucic Acids. YOSHIMIZU TOYAMA (*J. Chem. Ind. Japan*, 1922, 25, 1053—1055).—*Methyl behenate* separates from alcohol in lustrous scales, m. p. 54—54.5°, b. p. 224—225°/5 mm. Ethyl behenate forms fine, microcrystalline granules from alcohol, m. p. 50—50.5°, b. p. 230—231°/5 mm. Behenamide, fine needles, m. p. 111—112°. *Behenamide*, fine needles, m. p. 101—102°.

Methyl erucate is a nearly colourless liquid, d^{15}_4 0.8735, d^{20}_4 0.8702, n^{15}_D 1.4577, n^{20}_D 1.4558, b. p. 221—222°/5 mm. Ethyl erucate is a nearly colourless liquid, d^{15}_4 0.8676, d^{20}_4 0.8648, n^{15}_D 1.4562, n^{20}_D 1.4543, b. p. 229—230°/5 mm. Erucamide forms fine needles, m. p. 82.5—83°. *Erucanilide* forms lustrous scales, m. p. 65.5—66°.

K. K.

Electro-synthesis of Azelaic and Thapsic Acids. MABEL CARMICHAEL (T., 1922, 121, 2545—2549).

Oxidation of some Sugar Acids. WILHELM GREINERT (*Annalen*, 1922, 429, 152—163).—An examination of the space formula of mucic acid shows that when this is oxidised in such a way as to eliminate two adjacent carbon atoms as oxalic acid, the residue should appear as racemic acid, but that if one carbon atom is removed from each end of the chain, the residue should be obtained as *i*-tartaric acid. Experiment shows that the tartaric acid obtained on oxidation by alkaline permanganate is racemic acid unaccompanied by any appreciable trace of *i*-tartaric acid.

Similarly, *d*-saccharic acid on oxidative fission could give oxalic acid and *i*-tartaric acid, oxalic acid and *d*-tartaric acid, or two molecules of carbon dioxide and *l*-tartaric acid. Experiment showed the presence of racemic acid mixed with *d*-tartaric acid, but no *i*-tartaric acid, in the oxidation product.

Mannosaccharic acid should give *i*-tartaric acid and oxalic acid, or *l*-tartaric acid and two molecules of carbon dioxide. Probably the reaction takes the former course, although no undoubted specimen of *i*-tartaric acid was isolated; for direct experiment shows that this acid is destroyed by permanganate more readily than *l*-tartaric acid, and that, under the conditions used in oxidising mannosaccharic acid, added *i*-tartaric acid could not be recovered from the product.

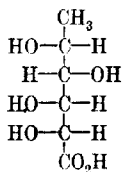
C. K. I.

Chemistry of the Sugars. IV. H. KILIANI (*Ber.*, 1922, 55, [B], 2817—2826; cf. A., 1921, i, 304; this vol., i, 223, 321).—The technique of the oxidation of sugars and polyhydroxy-acids at the atmospheric temperature by nitric acid is improved further by removing any excess of nitric acid by agitating the solution, after dilution, if necessary, with five or six portions of ether (each one and

a half times the volume of the solution). The sixth extract is usually free from nitric acid. The aqueous solution may still contain nitric esters. It is allowed to remain exposed to the air for twelve to twenty-four hours to permit the dissolved ether to evaporate and is then concentrated, if necessary, in a vacuum over sulphuric acid. The nitric esters during this period become hydrolysed gradually, and the liberated nitric acid causes a fresh oxidation. For the sake of safety, the ethereal extracts are immediately transferred to a bottle containing sodium hydroxide solution (1 in 3). The efficiency of the process is illustrated by the identification of *l*-trihydroxyglutaric acid as a by-product of the preparation of ketorhamnonolactone and by the preparation of *r*-pentahydroxypimelic acid from α -glucoheptonic acid [quinine pentahydroxypimelate crystallises in long, lustrous needles (+ 4H₂O); the brucine salt (+ 6H₂O) forms microscopic rods].

The strongly reducing acid which has been isolated from the products of the oxidation of dextrose and *d*-gluconic acid with nitric acid (A., 1921, i, 304; this vol., i, 223) is identified as 5-keto-*d*-gluconic acid, which has been described previously by Boutroux and Bertrand (A., 1904, ii, 760). It is conveniently obtained as its calcium salt by precipitation of the strongly acetic acid solution with calcium chloride when it separates before the calcium saccharate. The identity of the acid with Bertrand's product is established by the crystallographical examination of the calcium and cadmium salts. 5-Keto-*d*-gluconic acid gives a semicarbazone-semicarbazide C₈H₁₃O₈N₂, microscopic needles which become discoloured at about 170°, and soften without actually melting at about 200°.

Constitution of Ketorhamnonic Acid.—This acid has been described previously (this vol., i, 223) as an α -keto-compound. The ease with which, in comparison with rhamnose, it yields iodoform suggests that the carbonyl and methyl groups are directly attached to one another, and that it is therefore a δ -keto-substance. This view is strengthened by the occurrence of *l*-trihydroxyglutaric acid among the products of its oxidation (see above), and confirmed by its behaviour when reduced with sodium amalgam, when, in place of *l*-isorhamnonic acid, which would be expected from an α -keto-compound, it yields a new acid, *l*-guleonic [δ -epi-*l*-rhamnonic] acid (annexed formula). *l*-Guleonolactone crystallises in rods or large plates with apparent rectangular bases



m. p. 152°. It has $[\alpha]_D -84.9^\circ$ or -87.7° initially in aqueous solution, which diminishes as the lactone becomes hydrated into the acid. The calcium, sodium, and barium salts are amorphous; the brucine salt (+ 7H₂O) crystallises in coarse plates. The phenylhydrazone forms coarse needles, m. p. 153°; the hydrazide, m. p. 155–156°, has $[\alpha]_D +15.2^\circ$ in aqueous solution, the sign of the rotation in accordance with Hudson's rule, proving definitely that *l*-isorhamnonic acid is not present.

Lævulosecarboxylic Acid.—The isolation of a levorotatory phenylhydrazone of lævulosecarboxylic acid, m. p. 187°, $[\alpha]_D -29.5^\circ$

in aqueous solution, is directly contradictory to Nef's assumption with regard to the position of the α -hydroxy-group (A., 1910, i, 711). More recent observation renders it exceedingly improbable that the addition of hydrocyanic acid to laevulose is completely unsymmetrical; it is more probable that two acids are formed simultaneously.

H. W.

A Highly Unsaturated Hydrocarbon, and some Higher Alcohols in a Commercial Illipé Fat. SHŪMEI KOBAYASHI (*J. Chem. Ind. Japan*, 1922, 25, 1188—1196).—A new, highly unsaturated hydrocarbon, *illipene*, $C_{30}H_{50}$, a light yellow solid with an aromatic odour, m. p. 64.5° , iodine value 382.5, was isolated from the unsaponifiable matter (8.55% of the fat) of a commercial illipé fat imported from India. It is optically inactive and boils at $315^\circ/2.5$ mm. The *hydrochloride* is a white powder, m. p. 115 — 116° . The unsaponifiable matter also contains four higher alcohols which were separated by repeated recrystallisation from acetone: (I) $C_{21}H_{42}O$, microscopic, silky needles, m. p. 196 — 197° , iodine value, 114.9° ; (II) $C_{23}H_{46}O$, silver-white crystals, m. p. 186 — 186.5° , iodine value, 100.2; (III) $C_{27}H_{54}O$, silver-white grains, m. p. 159 — 160° , iodine value 82.3, and (IV) $C_{31}H_{62}O$, light yellow needles, m. p. 125 — 135° , iodine value 100.2. The solid mixture of fatty acids of the fat is mainly composed of stearic acid. K. K.

The Drying of Fatty Oils. PAWEŁ ŚLANSKY (*Z. angew. Chem.*, 1922, 35, 389—391).—The drying of linseed oil is produced by oxidation and gelatinising processes, the latter being favoured by increase in temperature. The oxidation of linseed oil fatty acids proceeds more rapidly than that of linseed oil itself, and the oxidation of the oil is accelerated by the addition of linolic acid or linolenic acid. Gelatinisation of the oil is increased by the addition of oleic acid. The solid product, "linoxyn," obtained when linseed oil dries, is capable of absorbing 15% of its weight of water.

W. P. S.

Composition of the Fatty Acids of Rape Oil. YOSHIYUKI TOYAMA (*J. Chem. Ind. Japan*, 1922, 25, 1044—1053; cf. *J. Tokyo Chem. Soc.*, 1895, 16, 187).—The main constituent of the fatty acids of rape oil obtained from the seeds of *Brassica campestris*, L. (*B. chinensis*, L.), grown in the Shiga prefecture, was erucic acid (about 65%). The saturated acids (less than 2%) consisted of palmitic acid with seemingly stearic, behenic, lignoceric, and arachidic acids. The presence of linolenic, linolic, and oleic acids was proved from the bromination and oxidation of the liquid acids and their methyl esters. [*Cf. J. Soc. Chem. Ind.*, 1922, Dec.] K. K.

Stereochemical Studies. VI. Stereoisomeric Trithiocarbolactonic Acids. BROR HOLMBERG (*Arkiv Kem. Min. Geol.*, 1921—1922, 8, No. 8, 1—17).—The action of potassium trithiocarbonate on an α -bromopropionate yields two stereoisomeric trithiocarbolactonic acids (A., 1905, i, 323). That the isomeride with the higher melting point is the racemic modification is shown by unpublished work of the author and Ramberg, who, by using

highly active α -bromopropionic acid, obtained active trithiocarbolactic acids. By means of *d*- and *l*- α -phenylethylamines (Lovén, A., 1905, i, 875), the author has now succeeded in resolving the racemic acid into its components. The inactive isomeride with the lower melting point represents the meso-form.

meso-Trithiocarbolactic acid, $\text{CS}(\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{H})_2$, forms crystals, m. p. $104\text{--}105^\circ$, its saturated aqueous solution containing 27.4 grams per litre at 25° ; its crystalline barium salt ($+5\text{H}_2\text{O}$) was prepared. An attempt to prepare an aniline hydrogen salt yielded 3-phenyl-5-methylrhodanine (A., 1910, i, 361), and attempts to obtain *d*- α -phenylethylamine and *d*- α -phenylethylamine hydrogen salts resulted in the formation of *l*-di- α -phenylethylthiocarbamide, $\text{CS}(\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{Na})_2 + \text{CHPhMe}\cdot\text{NH}_2 = \text{SH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Na} + \text{CO}_2\text{Na}\cdot\text{CHMe}\cdot\text{S}\cdot\text{CS}\cdot\text{NH}\cdot\text{CHPhMe}$, and the latter $+ \text{CHPhMe}\cdot\text{NH}_2 = \text{CO}_2\text{Na}\cdot\text{CHMe}\cdot\text{SH} + \text{CS}(\cdot\text{NH}\cdot\text{CHPhMe})_2$ (cf. Lovén and Ohlsson, A., 1914, i, 830); thiolactic acid is also formed, $\text{CS}(\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{Na})_2 + 2\text{H}_2\text{O} = 2\text{CO}_2\text{Na}\cdot\text{CHMe}\cdot\text{SH} + \text{CO}_2 + \text{H}_2\text{S}$.

d-Trithiocarbolactic acid forms small, yellow prisms, m. p. $150\text{--}151^\circ$ on slow, or $154\text{--}155^\circ$ on rapid, heating; its saturated aqueous solution contains 3.04 grams per litre at 25° . Its readily soluble barium salt ($+4\text{H}_2\text{O}$); aniline hydrogen salt, $2\text{C}_6\text{H}_5\text{O}_4\text{S}_2\text{NHPh}$, yellow, crystalline crust, m. p. $134\text{--}135^\circ$, and aniline salt, $\text{C}_{19}\text{H}_{24}\text{O}_4\text{N}_2\text{S}_3$, yellow, crystalline powder, m. p. 135° (gas evolution), were prepared.

d-Trithiocarbolactic acid crystallises in small, yellow prisms, m. p. $136\text{--}136.5^\circ$, $[\alpha]_D^{20} +167.4^\circ$ in acetone, $+166.1^\circ$ in absolute alcohol, and $+187.9^\circ$ in ethyl acetate. As sodium hydrogen salt $[\alpha]_D^{20}$ for the acid is $+80.9^\circ$ and as sodium salt $+50.6^\circ$.

The *l*-isomeride shows the same melting point and solubility as the *d*-compound; $[\alpha]_D^{20} -167.8^\circ$ in acetone and -109° in water. When heated in aqueous solution, the acid gradually becomes inactive.

When heated with ammonia, *d*-trithiocarbolactic acid yields a dextrorotatory thiolactic acid which is converted into a dextrorotatory dithiodilactic acid when oxidised (cf. Lovén, A., 1908, i, 714).
T. H. P.

The Properties of Dibenzoylcystine. CHARLES GEORGE LEWIS WOLF and ERIC KEIGHTLEY RIDEAL (*Biochem. J.*, 1922, 16, 548–555).—Gels of dibenzoylcystine may be prepared by peptisation with hot water. The substance is a relatively strong acid with a dissociation constant of 1.49×10^{-3} . The gel structure appears to be fibrillary and relatively coarse. The sodium salt of the acid exhibits no gelatinising properties. The presence of acids greatly reduces the solubility of the compound. This was confirmed by observations on the water-retaining capacity and internal viscosity of the gel. Lyotropic salts, such as ammonium thiocyanate, reduce the water-retaining power of the gel, producing ultimate liquefaction. Kationic dyes are adsorbed and precipitated by the gel. Anionic dyes diffuse in a normal manner, whilst halogen dyes apparently react chemically with the sulphur group. Di-

nitrobenzoyl cystine has similar properties to the simple compound. A possible structure for the gel fibril based on the effect of chemical substitution on the gel formation is suggested.

S. S. Z.

Preparation of Crotonaldehyde. CONSORTIUM FÜR ELEKTRO-CHEMISCHE INDUSTRIE G. M. B. H. (D.R.-P. 349915; from *Chem. Zentr.*, 1922, iv, 43).—Acetaldehyde vapour is passed over suitable catalysts at temperatures below 300°. The crotonaldehyde is removed at once from the seat of the reaction with the excess of unchanged acetaldehyde which is led back again into the reaction chamber, after separation from the crotonaldehyde. Charcoal coated with titanium oxide or moulds made of aluminium oxide or hydroxide, beryllium oxide, calcium hydroxide, bog iron ore, cement, or mixtures of these substances are used as catalysts.

G. W. R.

Synthesis of Substances resembling Disaccharides from Monohydroxyaldehydes. BURCKHARDT HELFERICH and RUDOLF WEIDENHAGEN (*Ber.*, 1922, 55, [B], 3348—3354).—In continuation of the examination of γ - and δ -hydroxyaldehydes which have been shown to exhibit a close analogy to the aldoses, it is found that they can be converted by boiling their ethereal solutions with dehydrated copper sulphate into products which are very similar to a disaccharide of the type of trehalose.

γ -Hydroxyvaleraldehyde is converted into *di- γ -hydroxyvaleraldehyde* [*bis-5-methyltetrahydro-2-furyl ether*], $\text{O}(\text{CH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} - \text{CHMe}_2 \end{smallmatrix})_2$, a colourless, mobile liquid, b. p. 86—92°/11 mm., d_4^{25} 1.0107, n_D^{25} 1.4409. It is sparingly soluble in water (1:55). It does not reduce boiling Fehling's solution or exhibit any reaction of a free aldehyde group. It does not evolve methane when treated with magnesium methyl iodide according to the method of Tschugacev and Zerewitinov. It is very smoothly hydrolysed by dilute acids with the production of two molecular proportions of γ -hydroxyvaleraldehyde.

γ -Hydroxy- γ -methylhexaldehyde is transformed in a similar manner into *di- γ -hydroxy- γ -methylhexaldehyde* [*bis-5-ethyl-5-methyltetrahydro-2-furyl ether*], $\text{O}(\text{CH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} - \text{CMeEt}_2 \end{smallmatrix})_2$, a colourless liquid with a pleasant odour and bitter, resinous taste, b. p. 121—125°/11 mm., d_4^{25} 0.9678, n_D^{25} 1.4447. It is very sparingly soluble in water (1:100). In its chemical properties, it resembles its simpler homologue.

Di- δ -hydroxy- α -hexaldehyde, [*bis-6-methyltetrahydro-2- α -pyryl ether*] $\text{O}(\text{CH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} - \text{CHMe} \end{smallmatrix} > \text{CH}_2)_2$, is a colourless, fairly mobile liquid, b. p. 100—105°/11 mm., d_4^{25} 1.000, n_D^{25} 1.4480; one part of it dissolves in sixty parts of water.

H. W.

The Oxidation of Acetone with Potassium Permanganate. WILLIAM LLOYD EVANS and LILY BELL SEFTON (*J. Amer. Chem. Soc.*, 1922, 44, 2276—2283; cf. this vol., i, 1108).—By the oxidation

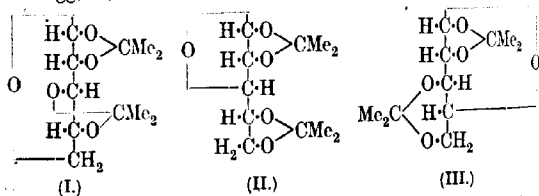
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of acetone with neutral or alkaline potassium permanganate at 25°, 50°, and 75°, the sole products are oxalic and acetic acids and carbon dioxide. The yield of oxalic acid increases with increase both in the temperature and the concentration of the alkali, whilst that of acetic acid diminishes with decrease in the temperature and increase in the concentration of the alkali. The production of carbon dioxide increases with rise in temperature. Acetic acid and carbon dioxide arise from the oxidation of acetaldehyde and methylene, respectively. The production of oxalic acid in neutral solutions is due to the very slow oxidation of acetic acid and the oxidation of vinyl alcohol. The results indicate that in aqueous solution acetone must be in equilibrium with isoacetone, an increase in the alkalinity causing an increase in the formation of isoacetone. Confirmation of Witzemann's view as to the intermediate production of acetylcarbinol in the oxidation of acetone is given (cf. A., 1918, i, 58). W. G.

Researches on Residual Affinity and Co-ordination. IX. Interaction of Selenium Tetrachloride and β -Diketones. GILBERT T. MORGAN, HARRY DUGALD KEITH DREW, and THOMAS VIPOND BARKER (T., 1922, 121, 2432—2473).

Optical Rotations of the Sugars. I. The Aldohexoses and Aldopentoses. JOHN GWILLIAM MALTBY (T., 1922, 121, 2608—2612).

Acetone Sugars. II. Diacetonyxylose. KARL FREUDENBERG and OLAV SVANBERG (*Ber.*, 1922, 55, [B], 3239—3242).—Diacetonyxylose is of particular interest with regard to the relation of its existence to the structure of diacetoneglucose, since xylose has the same configuration as dextrose but lacks the carbon atom. The isolation of the compound therefore demonstrates that the carbon atoms in dextrose are in themselves capable of combining with two isopropylidene groups, and, although not in itself affording proof that this is actually the case, confirms the possibility that dextrosediactone has position 6 unsubstituted (cf. Irvine and Hogg, T., 1914, 105, 1386).



Diacetonyxylose (formulae I, II, or III), a colourless, viscous liquid, b. p. 85—87°/0.5 mm., is prepared by the action of hydrogen chloride on a mixture of finely-divided xylose and anhydrous acetone. In freshly prepared aqueous solution it has $[\alpha]_D +13.8^\circ$, which, after a day, attains a constant value, -1.3° . A specimen which has been preserved for about ten days has an initial specific

rotation about half as great as that of the freshly prepared material under similar conditions. When prepared in this manner, a portion of the hydrogen chloride is retained in organic combination (but lost during the distillation); it appears to exist in an intermediate compound which could not be isolated. In the condensation, hydrogen chloride may be replaced by naphthalene- β -sulphonic acid, but the yields of the products are not quite so good.

H. W.

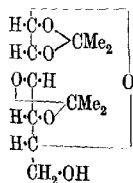
Carbohydrates. II. A New Anhydride ($\alpha\beta$) of Glucose.

PERCY BRIGL (*Z. physiol. Chem.*, 1922, **122**, 245—262; cf. this vol., i, 225).—When α -chloro- $\gamma\epsilon\zeta$ -triactetylglucose is treated in benzene solution with ammonia, hydrogen chloride is removed with the formation of $\gamma\epsilon\zeta$ -triactetylglucose- $\alpha\beta$ -anhydride, white prisms, soluble in the usual organic solvents except light petroleum and carbon disulphide, m. p. 59.5°, $[\alpha]_D^{25} +106.5^\circ$. The heat of combustion is 1595 cal. With acetic anhydride, it reacts readily, and from the product, (α)-penta-acetylglucose can be isolated, m. p. 115°. With water, it yields a mixture of the (α) and (β) forms of $\gamma\epsilon\zeta$ -triactetylglucose. (α)- $\gamma\epsilon\zeta$ -Triactetylglucose forms fine needles, m. p. 113—115°, $[\alpha]_D^{25} +139.6^\circ$. With methyl alcohol, only $\gamma\epsilon\zeta$ -triactetyl- α -methylglucoside is formed, compact needles, m. p. 96—98°, $[\alpha]_D^{25} +9.4^\circ$.
W. O. K.

W. O. K.

Acetone Sugars. I. Transformations of Diacetoneglucose.

KARL FREUDENBERG and FRITZ BRAUNS (*Ber.*, 1922, 55, [B], 3233-3238).—Toluene-*p*-sulphonyldextrosediacetone (Freudenberg and Ivers, this vol., i, 523) is unusually stable towards alkalis, and is only slowly converted by boiling hydrazine into *hydrazino-tiacetoneglucose*, $C_{12}H_{22}O_5N_2$; m. p. 96–97°, $[\alpha]_D^{25}$ yellow +83.4° in water, $[\alpha]_D^{25}$ yellow +163.6° in acetone. When oxidised, diacetoneglucose is re-formed from it in small amount, so that it appears that the carbonyl group of the sugar and the union of the *isopropylidene* groups have remained unchanged. It is, however, remarkable that the hydroxy-group of dextrosediacetone after displacement by the hydrazine residue and re-formation by oxidation of the hydrazino-compound should return to its original spatial position in the molecule, and it is therefore tentatively suggested that the change would be more readily explicable if the hydroxy-group were regarded as attached to the 6-carbon



atom and the annexed formula were ascribed to diacetonoglucosose. Hydrizynediactoneglucosose is converted by benzaldehyde in the presence of ether into the corresponding benzylidene compound, $C_{19}H_{26}O_5N_2$, prisms, m. p. 99–100°, $[\alpha]_D^{20}$ yellow +144.2° in *s*-tetrachloroethane. The mother-liquors from the benzylidene derivative contain an unsaturated compound, *diactone-glucosose*, $C_{12}H_{18}O_5$, needles, m. p. 51°, $[\alpha]_D^{20}$ yellow +21.56° in absolute alcohol which is smoothly reduced by hydrogen in the presence of methyl acetate and spongy platinum to *diactonedecarglucosose*, $C_{12}H_{20}O_5$, m. p. 80°, $[\alpha]_D^{20}$ yellow

—34·60° in absolute alcohol, $[\alpha]_{\text{D}}^{20}$ yellow—61·9° in aqueous solution. Toluene-*p*-sulphonyldiacetoneglucose is reduced by sodium amalgam and ethyl alcohol (80%) to diacetoneglucose and toluene-*p*-sulphinic acid.

•• H. W.

The Acetone [isoPropylidene] Compound of Anhydroenneaheptitol. The Acetone Compounds of Polyhydroxy-alcohols. C. MANNICH and W. BROSE (*Ber.*, 1922, 55, [B], 3155—3157).—Anhydroenneaheptitol, obtained by the condensation of acetone and formaldehyde in the presence of calcium hydroxide, and to which the annexed formula is ascribed, readily yields a *diacetone* compound, $\text{C}_{15}\text{H}_{26}\text{O}_6$, leaflets, m. p. (indefinite) 229°. The substance still contains a free hydroxyl group, since it is converted by acetic anhydride and sodium acetate into a *monoacetate*, highly refractive needles, m. p. 140° (corr.). The formation of an acetone derivative is the more remarkable since the parent substance is a 1:3-glycol; it has been assumed previously (cf. Fischer, A., 1920, i, 807; Fischer, Bergmann, and Barwind, A., 1920, i, 805) that acetone derivatives are only obtainable from polyhydroxy-alcohols which have the hydroxy-groups attached to adjacent carbon atoms.

H. W.

Tetralævoglucosan and Tetraglucosan. HANS PRINGSHEIM and KARL SCHMALZ (*Ber.*, 1922, 55, [B], 3001—3007).—The polyamyloses, obtained by the fermentation of starch and glycogen with *Bacillus macerans*, are characterised by undergoing depolymerisation to their fundamental substances when acetylated by acetic anhydride in the presence of zinc chloride and by the impossibility of their complete methylation. These properties are not shown by polymeric anhydro-sugar, since tetralævoglucosan and tetraglucosan can be acetylated under similar conditions without undergoing depolymerisation, and are completely methylated with unexpected ease.

Lævoglucosan and tetralævoglucosan are prepared by a modification of the methods of Pictet and his co-workers (A., 1918, i, 59, 527; 1921, i, 766); the specific rotation of the latter substance could not be raised beyond +85°, whereas Pictet records +100°. Tetralævoglucosan is converted by acetic anhydride in the presence of a little zinc chloride into *tetralævoglucosan dodecaacetate*, $\text{C}_{48}\text{H}_{64}\text{O}_{32}$, an amorphous substance which is completely molten at 125° after softening at 108—109°; it has $[\alpha]_{\text{D}}^{20} +69\cdot59^\circ$ in glacial acetic acid solution. *Dodecamethyl tetralævoglucosan*, $\text{C}_{38}\text{H}_{64}\text{O}_{20}$, a pale yellow, viscous liquid, which does not reduce Fehling's solution, is readily prepared by two consecutive treatments of the parent substance with methyl sulphate and sodium hydroxide at 70°. It is hydrolysed by boiling dilute sulphuric acid (6%) to tetramethylglucose (identified as the anilide; m. p. 136—137°) and a dimethylglucose, whereby it is established that in the polymerisation of lævoglucosan, the rupture of the 1:6-oxygen bridge with formation of a free 6-hydroxy-group has occurred in two of the four molecules of the parent substance.

Tetraglucosan dodeca-acetate is an amorphous, hygroscopic substance, $[\alpha]_D^{25} + 70.82^\circ$ when dissolved in glacial acetic acid. *Dodecamethyltetraglucosan* is hydrolysed to tetramethylglucose, and two products which are characterised by solubility in anhydrous ether in the one case and in acetone in the other case.

Tetraglucosan octa-acetate has m. p. $84-86^\circ$, in agreement with the observations of Pictet (*loc. cit.*).

H. W.

Polysaccharides. XVI. P. KARRER [with W. FIORONI] (*Ber.*, 1922, 55, [B], 2854-2863; cf. this vol., i, 435).—The heats of combustion of the amyloses have been redetermined with the following results expressed in calories per gram of substance: diamylose (4285), α -tetra-amylose (4196), α -octa-amylose (4620), β -hexa-amylose (4166), *lavoglucosan* (4181), triamylose (identical with β -hexa-amylose) (4162.5). Polymerisation proceeds exothermally from diamylose to α -tetra-amylose and then strongly endothermally to octa-amylose. In further examination of the possibility of calculating the heat of combustion of a sugar of the general formula $(C_6H_{12}O_6)_n - (n-1)H_2O$, the values have been determined experimentally for cellobiose (3944) (calculated from the observed value for a specimen containing 2.2% of water), sucrose (3945), lactose (3953), and maltose (3949); within the limits of experimental error, these disaccharides, $C_{12}H_{22}O_{11}$, have identical heats of combustion. This is also true of maltose octa-acetate (4468) and cellobiose octa-acetate (4471). The observed and calculated values for the trisaccharide, raffinose, have been shown to be in harmony, and similar observations are recorded for the tetrasaccharide, stachyose (observed 4065; calculated, 4058).

The dependence of the heat of combustion on the degree of polymerisation is illustrated in the case of the α -amyloses. A comparison of the heats of combustion of acetyl-cellulose, -starch, and -inulin on the one hand and the non-acetylated polysaccharides on the other should therefore give valuable information as to the possibility of acetylation being accompanied by depolymerisation. The observed values are as follows: inulin (4190), starch (4182), cellulose (4185), starch hexa-acetate (4499), cellulose hexa-acetate (4496), inulin triacetate (4522). The heats of combustion of the acetates are calculated from those of the parent substances on the assumption that the heat of esterification (known to be small) can be neglected. The observed and calculated values agree so closely that there is no reason to suppose that an alteration of the degree of polymerisation of the carbohydrate occurs during acetylation.

The author has shown that hexa-amylose is identical with triamylose and his observations have been confirmed by the crystallographical measurements of Miggle and Johnson. The individuality of the substances has, however, been maintained by Pringsheim (this vol., i, 633), to whose arguments a critical reply is now given. Pringsheim's doubt as to the identity of the maltose hepta-acetate obtained by the action of acetyl bromide on triamylose is unjustified since it is a well-defined, crystalline substance. Attempts

to repeat the preparation of triamylose sodium hydroxide according to Pringsheim's method gave a product which contains sodium ethoxide. Contrary to Pringsheim's observations, the solubilities of triamylose and hexa-amylose in water are identical, and the observed discrepancies are due to the inadequacy of Pringsheim's method of experiment. With regard to Pringsheim's observation that the molecular weight of acetylated hexa-amylose is identical with that required for an acetylated triamylose, the author points out that acetylated anhydro-sugars are not in general suitable for determinations of molecular weight; incidentally, the molecular weight of acetylated hexa-amylose as determined by Rast's method (this vol., ii, 421) is about 1950 (or exactly double that found by Pringsheim). Doubts are cast on the individuality of Pringsheim's trifructose.

H. W.

The Absorption of Iodine by Starch. H. VON EULER and KARL MYRBÄCK (*Arkiv Kem. Min. Geol.*, 1922, 8, No. 9, 1—29; cf. this vol., i, 527).—Measurements have been made of the distribution of iodine between benzene and a solution of starch. Evidence is found of the existence of two compounds of iodine and potato starch, to which the formulæ $(C_6H_{10}O_5)_{18}I_2$ and $(C_6H_{10}O_5)_{18}I_4$ are given. Soluble starch has less affinity for iodine than potato starch, and there is more iodine in the benzene layer. There is evidence that hydrogen iodide is not necessary for the formation of the blue colour and that the compound of Mylius containing hydrogen iodide or potassium iodide is a further additive compound.

W. O. K.

Oxidation of Amylodextrin. WIKTOR SYNIEWSKI (*Roczniki Chem.*, 1922, 2, 83—94).—When amylodextrin (soluble starch) is oxidised by means of bromine in the presence of barium carbonate (to prevent the hydrolysis of the molecule), amyloextrinic acid, $C_{216}H_{348}O_{198}$, is obtained as a white, non-crystalline substance. It has an acid reaction, $[\alpha]_D^{20} + 191.09^\circ$, and its reducing power is 23.24% of that of maltose. In solution, it reduces alkaline silver solution and gives the "Molisch" reaction with α -naphthol, but the colour is not violet as with starch and the sugars, but carmine-red. In concentrated solution, it gives a red colour on warming with hydroxylamine hydrochloride and potassium hydroxide. The author assumes that amyloextrin has the formula $C_{216}H_{372}O_{186}$ and contains twelve maltose residues connected together by the carbonyl groups, and that the CH_2OH groups alone undergo oxidation to carboxyl groups.

W. T.

Some Physical Properties of Cotton Cellulose and its Modifications. A Summary of Existing Data. GEO. E. COLLINS (*Trans. Text. Inst.*, 1922, 13, 204—213).—The following subjects are dealt with: specific gravity, elasticity, specific inductive capacity, electrification, mechanical absorption of liquids, thermal effects accompanying water adsorption, changes resulting from the action of heat and cold, thermal conductivity, specific heat, heat of combustion, heat of reaction, refractive index, double

refraction and appearance in polarised light, action of ultra-violet light, optical activity of sols, ultra-microscopy, evidence of X-rays on structure. Data dealing with the swelling of cellulose and the adsorption of vapour by cellulose will be summarised in future reports, but it may be taken that little or nothing has been published about properties not included in the above list. J. C. W.

The Viscosity of Cellulose. II. The Lowering of the Viscosity of Cellulose by Various Reagents. REGINALD ARTHUR JOYNER (T., 1922, 121, 2395—2409).

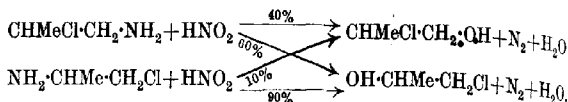
"Oxycellulose:" its Formation and Reactions. PERRY HERBERT CLIFFORD and ROBERT GEORGE FARGHER (*Trans. Text. Inst.*, 1922, 13, 189—204).—A review of the various methods of oxidation of cellulose, and the reactions of, and tests for, "oxycellulose," together with a bibliography. J. C. W.

Ligninsulphonic Acids. R. H. MCKEE and GEO. BARSKY (*Paper Trade J.*, 1922, 74, 46—48).—An attempt to separate the various acids by precipitation with calcium chloride. Three litres of sulphite waste liquor were concentrated to 800 c.c., filtered, and neutralised with calcium hydroxide. Calcium chloride was then added in quantities of 50 grams, the mixture being heated on the water-bath for two hours to induce coagulation; the precipitate was collected after each addition. Each fraction was then reprecipitated with calcium chloride from its solution in twice its weight of water. Analysis of the corresponding barium salts of the final fractions gave C 59.7—55.1%, H 6.4—5.9%. The ratio of carbon to hydrogen thus varies from 8.6 to 10.1, whilst the ratio for cellulose is 7. It is therefore considered that the substance contains several compounds of varying composition. CHEMICAL ABSTRACTS.

The Decomposition of Amines in the Vapour Stage. FRED W. URSON and LILA SANDS (*J. Amer. Chem. Soc.*, 1922, 44, 2306—2310).—When ethylamine vapour is passed over kaolin at 700° the chief products are ammonia, hydrogen cyanide, and a substance which is probably acetonitrile, together with smaller quantities of hydrogen and nitrogen. At 500°, no hydrogen cyanide is produced, a larger amount of ammonia is formed, and the gaseous products contain relatively larger amounts of unsaturated hydrocarbons. At 1000°, the nitrogen appears exclusively as free nitrogen, and much of the hydrogen as free hydrogen. The hydrocarbons are almost entirely saturated and to a large extent consist of butane. The decomposition of propylamine under similar conditions at 700° proceeds in a manner similar to that of ethylamine. The results may be explained on Nef's theory of methylenic dissociation (cf. *Annalen*, 1899, 309, 126; 1901, 318, 37). W. G.

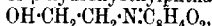
Kinetic Determinations of the Constitutions of Hydroxy- and Amino-chloropropanes. L. SMITH and B. PLATON (*Ber.*, 1922, 55, [B], 3143—3155).—The preparation of β -chloro-*n*-propylamine (cf. Gabriel and Ohle, A., 1917, i, 562) and α -chloro- β -aminopropane.

propane and their reactions with nitrous acid have been investigated. The latter changes are represented in the scheme :



It is therefore shown that a definite transformation can accompany the conversion of an amino- into a hydroxy-compound by means of nitrous acid even when the operation is conducted at a low temperature. The tendency towards transformation is most marked with the α -amino-compound. The reaction of an aliphatic amino-compound with nitrous acid should not therefore be used as a general method for the elucidation of constitution. The optically active " β -propylene chlorohydrin" described by Abderhalden and Eichwald (A., 1919, i, 2) must be regarded as a mixture of approximately equal quantities of the α - and β -compounds, the former of which is inactive; the corresponding propylene oxide and propylene glycol must also be partly inactive. The synthesis of $\alpha\beta$ -diglycerides from acylated γ -aminopropylene glycols (Bergmann, Brand, and Dreyer, A., 1921, i, 444) does not appear to rest on a firm theoretical basis.

The preparation of β -chloro- n -propylamine is effected according to the method of Gabriel and Ohle (*loc. cit.*); (the melting points observed for the various intermediate compounds by these chemists are recorded in brackets). Propylene oxide is converted by phthalimide into a mixture of β -hydroxyethylphthalimide,



lustrous leaflets, m. p. 129.5° (corr.), and β -hydroxy- n -propylphthalimide, prisms, m. p. 88° (corr.) [$90-91^\circ$, $88-89^\circ$]. The latter substance is converted into the corresponding chloride, b. p. $183-184^\circ/10$ mm., m. p. $97.5-98^\circ$ (corr.) [$100-102^\circ$], which is hydrolysed by glacial acetic and fuming hydrochloric acids to β -chloro- n -propylamine hydrochloride, m. p. 179° (corr.) [$183.5-186^\circ$]. The substance is, however, prepared more conveniently in quantity by the method of Abderhalden and Eichwald (*loc. cit.*). It is diazotised in faintly acid solution either as hydrochloride or tartrate; the chlorohydrin which is formed has b. p. $128-129.5^\circ$ and $128-129^\circ$, respectively, and is colourless, neutral, and free from aldehyde.

The preparation of α -chloro- β -aminopropane is effected by converting β -chloro- n -propylamine hydrochloride by means of sodium hydroxide into the imine, $\text{CHMe}\cdot\text{CH}=\text{NH}$, which is trans-

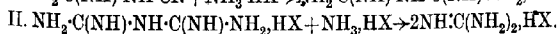
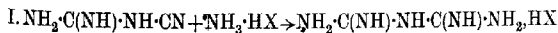
formed by concentrated hydrochloric acid into α -chloro- β -aminopropane hydrochloride; since the latter substance is hygroscopic and difficult to preserve, it is converted into the corresponding picrate, m. p. 146° , which is re-converted into the hydrochloride immediately before use. It is diazotised at $40-50^\circ$, giving a colourless, neutral chlorohydrin, b. p. 126° .

The composition of the mixture of chlorohydrins is established from measurements of its rate of decomposition by barium hydroxide. The bimolecular velocity coefficient for α -chloro- β -hydroxypropane for $t=0$ is $k_0=14.3$, whereas the corresponding constant for β -chloro- α -hydroxypropane is about 4. The coefficients of the mixtures lie intermediate between these values and decrease markedly as decomposition proceeds. The composition of the mixtures is calculated on the assumption that for a definite mixture the velocity coefficient at any instant is only dependent on the ratio of quantities of isomerides actually present at that instant.

The constitution of the chloropropylamines is established similarly by studying the rate of decomposition by barium hydroxide. The picrates are used, and the velocity of the change is determined by estimation of the chlorine by Volhard's method. α -Chloro- β -propylamine has $k=0.50$ at 25° , whereas the corresponding value for β -chloro- n -propylamine is 0.067. Since the action of chloroamines towards alkali hydroxide is similar to that of chlorohydrins, it is valid to assume that the compound which is most readily decomposed contains the halogen in the α -position. H. W.

The Action of Sodammonium on Hexamethylenetetramine, Tetramethyldiaminomethane, and Ethylidene-ethylamine. M. PICON (*Compt. rend.*, 1922, 175, 695—698; cf. Lebeau and Picon, this vol., i, 801).—Sodammonium is the only hydrogenating substance that is without action on hexamethylenetetramine, and it has no action on saturated aliphatic compounds which contain nitrogen. Its action on unsaturated aliphatic nitrogen compounds results in the formation of condensation products in which two molecules of the original substance are linked by the carbon atoms which were previously unsaturated. This reaction furnishes a new method of preparing secondary diamines. The inference is drawn that the inertness of sodammonium with respect to hexamethylenetetramine is due to the fact that the latter has no double bond which links carbon to nitrogen; this tends to support the constitutional formula suggested by Duden and Scharff (A., 1896, i, 122). H., J. E.

Mechanism of Guanidine Formation in Fused Mixtures of Dicyanodiamide and Ammonium Salts. J. S. BLAIR and J. M. BRAHAM (*J. Amer. Chem. Soc.*, 1922, 44, 2342—2352; cf. Davis, this vol., i, 117, 118; Werner and Bell, T., 1920, 117, 1133).—Experimental evidence is given in support of the view that the mechanism of guanidine formation in fused mixtures of dicyanodiamide and an ammonium salt consists first in the formation of the diguanide salt by the addition of the ammonium salt to the nitrile group of dicyanodiamide, and the subsequent addition of a second molecule of the ammonium salt to form two molecules of the guanidine salt.



When dicyanodiamide is fused with ammonium thiocyanate, the amount of diguanide thiocyanate in the fused mass increases at first with the time of fusion, then reaches a maximum, and slowly diminishes. On the other hand, guanidine thiocyanate does not make its appearance until the diguanide thiocyanate has nearly reached its maximum concentration.

When diguanide nitrate is fused with ammonium nitrate there is a decided formation of guanidine nitrate and the statement that diguanide salts are formed by the reverse of reaction II above is shown to be very doubtful.

The authors consider that the experimental results support the cyanoguanidine structure for dicyanodiamide.

W. G.

Mutarotation and Pseudo-mutarotation of Glucosamine and its Derivatives. JAMES COLQUHOUN IRVINE and JOHN CAMPBELL EARL (T., 1922, 121, 2370—2376).

Salicylidene Derivatives of α -Glucosamine. JAMES COLQUHOUN IRVINE and JOHN CAMPBELL EARL (T., 1922, 121, 2376—2381).

The Influence of Position and of Temperature on the Reaction of Aliphatic Amino-nitrogen with Nitrous Acid. MAX S. DUNN and CARL L. A. SCHMIDT (*J. Biol. Chem.*, 1922, 53, 401—410).—The rate at which nitrous acid deaminises aliphatic amino-acids depends on the position of the amino-group; the greater the distance of this from the carboxyl the more slowly the reaction proceeds. In all cases, a decrease in temperature causes a diminution in the rate, but, contrary to the statement of Sure and Hart (A., 1917, ii, 551) the deamination of the ϵ -amino-group of lysine is not completely inhibited at 1°. Casein is deaminised more slowly than lysine at the ordinary temperature. E. S.

The Synthesis of Glycine from Formaldehyde. ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI (*Biochem. J.*, 1922, 16, 702—703).—Methylenecarboxamidonitrile is prepared by Klages' method by condensing two molecules of formaldehyde with one molecule of ammonium cyanide. The nitrile is then hydrolysed with a boiling 40% solution of barium hydroxide and the methylene derivative of glycine formed is boiled until no more formaldehyde is given off. The yield of glycine from aldehyde by this method is 54% of the theoretical—the highest yield of glycine yet recorded as a result of its direct synthesis from formaldehyde.

S. S. Z.

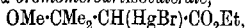
Hydrolysis of Glycylglycine by Hydrochloric Acid. IV. S. JAITSCHNIKOV (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 147—150).—Both at 10° and at 100°, the hydrolysis of glycylglycine by means of hydrochloric acid proceeds, for about one-third of its course, in accordance with the equation for a reaction of the first order (cf. Euler, A., 1907, i, 574).

T. H. P.

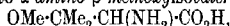
The Preparation of α -Amino- β -hydroxy-acids from Olefine Carboxylic Acids. WALTHER SCHRAUTH and HANNS GELLER (*Ber.*, 1922, 55, [B], 2783—2796).—The possible general applicability of a synthesis of α -amino- β -hydroxy-acids from ethylenecarboxylic acids on the following lines has been investigated: ester of olefinecarboxylic acid $\xrightarrow[\text{methyl alcohol}]{\text{mercury acetate}}$ β -methoxy- α -acetato-

mercuri-ester $\xrightarrow{\text{KBr}}$ β -methoxy- α -bromomercuri-ester $\xrightarrow{\text{bromine}}$ α -bromo- β -methoxy-ester $\xrightarrow{\text{hydrolysis}}$ α -bromo- β -methoxy-acid $\xrightarrow{\text{ammonia}}$ α -amino- β -methoxy-acid $\xrightarrow{\text{HBr}}$ α -amino- β -hydroxy-acid. The synthesis appears likely to be valuable in the purely aliphatic series, but complications follow when aromatic radicles are present.

Ethyl β -methoxy- α -bromomercuriisovalerate,



colourless plates, m. p. 51° , is prepared by treating ethyl β -dimethylacrylate with a solution of mercuric acetate in methyl alcohol during three days at the atmospheric pressure and subsequently adding an aqueous solution of potassium bromide to the mixture. It is slowly transformed by a solution of bromine in chloroform into *ethyl α -bromo- β -methoxyisovalerate*, a colourless liquid which is hydrolysed by $N/2$ -aqueous sodium hydroxide to *α -bromo- β -methoxyisovaleric acid*, $\text{OMe}\cdot\text{CMe}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, m. p. 77° . When the latter is heated with aqueous ammonia (25%) at 100° , it is transformed into *α -amino- β -methoxyisovaleric acid*,



colourless, lustrous plates, decomp. 250 — 260° , from which *α -amino- β -hydroxyisovaleric acid*, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}(\text{NH})\cdot\text{CO}_2\text{H}$, m. p. 218° (decomp.), is prepared by means of boiling hydrobromic acid (d 1.47). The latter acid is converted by phenylcarbimide into the compound, $\text{C}_{12}\text{H}_{16}\text{O}_4\text{N}_2$, m. p. 162° (decomp.); it gives a naphthalene- β -sulphonyl derivative, $\text{C}_{15}\text{H}_{17}\text{O}_5\text{NS}$, small, colourless needles, m. p. 261° .

Difficulties are encountered when the series of reactions is applied to methyl cinnamate (cf. Schrauth, Schoeller, and Struensee, A., 1910, i, 347). The preparation of methyl β -methoxy- α -bromomercuri- β -phenylpropionate, $\text{OMe}\cdot\text{CHPh}\cdot\text{CH}(\text{HgBr})\cdot\text{CO}_2\text{Me}$, is effected in good yield, but the replacement of the mercury complex by bromine occurs slowly in the presence of chloroform with simultaneous production of methyl α , β -dibromo- β -phenylpropionate, but rapidly in the presence of ethyl acetate, with formation of *methyl α -bromo- β -methoxy- β -phenylpropionate*. The hydrolysis of the latter is not very satisfactory, since considerable quantities of halogen-free products are obtained when sodium hydroxide is used, whereas α , β -dibromo- β -phenylpropionic acid is formed when hydrobromic acid is employed. Attempts are made to overcome the difficulties attendant on hydrolysis by the use of cinnamic acid as initial material. The latter is converted successively into *β -methoxy- α -bromomercuri- β -phenylpropionic acid*, m. p. 160 — 166° (decomp.), *α -bromo- β -methoxy- β -phenylpropionic acid*, m. p. (indefinite) 170° after softening at 165° (which appears to be a stereoisomide of the acid obtained in the above series, starting from methyl cin-

namate) and α -amino- β -methoxy- β -phenylpropionic acid, plates, m. p. 236° (decomp.) [corresponding compound from phenylcarbamide, colourless plates, m. p. 161° (decomp.); β -naphthalenesulphonyl derivative, prisms, m. p. 157°]. Replacement of the methoxy- by the hydroxy-group in the latter acid could not be effected by hydrobromic or hydriodic acids, bromohydrocinnamic and cinnamic acids being formed. α -Bromo- β -methoxy- β -phenylpropionic acid, prepared by the hydrolysis of methyl α -bromo- β -methoxy- β -phenylpropionate, crystallises in colourless needles, m. p. 126–127°.

Ethyl p -methoxycinnamate is converted in the usual manner into ethyl β -methoxy- α -bromomercuri- β - p -methoxyphenylpropionate, prismatic plates, m. p. 107°. The elimination of the mercury complex by bromine does not, however, follow a completely normal course, since bromination of the phenyl group occurs simultaneously, as is shown by the ultimate isolation of α -amino- β -methoxy- β - p -methoxybromophenylpropionic acid, pale yellow plates, m. p. 224° (decomp.) (the corresponding derivative from phenylcarbamide is described). On the other hand, ethyl β -methoxy- α -iodomercuri- β - p -methoxyphenylpropionate, m. p. 117°, is very slowly converted by iodine in ethereal solution into ethyl α -iodo- β -methoxy- β - p -methoxyphenylpropionate, a pale yellow liquid, which is hydrolysed by $N/2$ -sodium hydroxide solution to α -iodo- β -methoxy- β - p -methoxyphenylpropionic acid, $C_{11}H_{13}O_4I \cdot 2H_2O$, lustrous needles, m. p. 89–90°, in which, however, the iodine could not be replaced by the amino-group; all experiments with aqueous or liquid ammonia led to the formation of p -methoxycinnamic acid or the corresponding styrene. In one instance, however, the desired α -amino- β -methoxy- β - p -methoxyphenylpropionic acid, long plates, m. p. 233° (decomp.), was obtained in very small yield, but the experiment could not be repeated. H. W.

Synthesis of Aminohydroxy-acids and the Amino-acid from cycloPropyl Methyl Ketone (Acetyltrimethylene). N. D. ZELINSKY and E. F. DENGIN (*Ber.*, 1922, 55, [B], 3354–3361).—The synthesis of a series of hydroxyamino-acids from keto-alcohols by the cyanohydrin method is recorded (cf. Zelinsky and Stadnikoff, A., 1906, i, 425).

α -Amino- β -hydroxy- α -methylpropionic acid (α -methylserine), $OH \cdot CH_2 \cdot CMe(NH_2) \cdot CO_2H$, transparent platelets, m. p. 243° (decomp. in a sealed capillary), is prepared by the addition of acetylcarbinyl acetate (cf. Perkin, T., 1891, 59, 786) to an aqueous solution of potassium cyanide and ammonium chloride and treatment of the product of the reaction with hydrochloric acid; the yield is 12.6% of that theoretically possible. Better yields (41%) are obtained when acetylcarbinol is substituted for the acetate. The copper salt of α -methylserine, $(C_4H_8O_3N)_2Cu \cdot 2H_2O$, crystallises in small, blue needles.

Hydroacetylacetone, potassium cyanide, and ammonium chloride give α -amino- γ -hydroxy- α -methyl- n -valeric acid (α - β -hydroxy- n -propylalanine), $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CMe(NH_2) \cdot CO_2H$, small needles,

m. p. 232—233° (the crystalline, copper salt, $(C_6H_{12}O_3N)_2Cu, 2H_2O$, is described).

α -Amino- δ -hydroxy- α -methyl-n-valeric acid (α - γ' -hydroxy-n-propyl-alanine), $OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe(NH_2)\cdot CO_2H$, small needles, m. p. 198—200°, is similarly prepared from acetopropyl alcohol (a modified method for the preparation of this substance is described in detail); the corresponding copper salt is described.

α -Amino- ϵ -hydroxy- α -methyl-n-hexoic acid (α - δ -hydroxy-n-butylalanine), $OH\cdot CH_2\cdot [CH_2]_3\cdot CMe(NH_2)\cdot CO_2H$, prepared from δ -aceto-n-butylalcohol, crystallises in small platelets, m. p. 224—226°; the copper salt, $(C_7H_{14}O_3N)_2Cu, 2H_2O$, is a blue, crystalline powder.

α -Amino- α -cyclopropylpropionic acid (α -cyclopropylalanine), $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > CH\cdot CMe(NH_2)\cdot CO_2H$, prepared from acetylcyclopropane, crystallises in needles, m. p. 273—275°, in a closed capillary; it sublimes readily at about 125°. The corresponding hydrochloride and copper salt, $(C_6H_{10}O_2N)_2Cu, 2H_2O$, bluish-violet plates, are described.

H. W.

Catalysis of the Formation and Hydrolysis of Acetamide by Acetic Acid. WILLIAM A. NOYES and WALTER F. GOEBEL (*J. Amer. Chem. Soc.*, 1922, **44**, 2286—2295).—Acetic acid acts as a catalyst both for the formation of acetamide from ammonium acetate and for the hydrolysis of acetamide by water. The hydrolysis of acetamide by water is autocatalytic, probably because the acetic acid from the dissociation of the ammonium acetate formed catalyses the subsequent reaction.

The formation of acetamide from ammonium acetate with or without the addition of 0.1 mol. of acetic acid is essentially a bimolecular reaction between ammonia and acetic acid. In all probability an intermediate compound, $CH_3C(OH)_2\cdot NH_3$, is formed as a passing phase in the reaction. The formation and hydrolysis of acetamide in the presence of 1.5 mols. of acetic acid is chiefly a bimolecular reaction with one of the constituents, hydrogen-ion or acetic acid, constant. The other constituents limiting the speed of the reaction must be ammonia on one side, and acetamide on the other.

In the preparation of acetamide a practically quantitative yield is obtained if equimolecular proportions of ammonium acetate and glacial acetic acid are heated together at just below the boiling point of the mixture for thirty to fifty minutes and then the mixture is slowly distilled through a good fractionating column the temperature at the top of which is not allowed to exceed 103—104°. In this way a residue of acetamide, b. p. 215—217°, is obtained.

W. G.

The Compounds of Carbamide and Benzoic Acid. YUKIOCHI OSAKA and KINJI ANDO (*Mem. Coll. Sci. Kyōto*, 1922, **5**, 169—172).—The solubility of mixtures of carbamide and benzoic acid in alcohol have been determined at 0°, 25°, and 40°, and no evidence was found for the existence of any compound of the two.

W. E. G.

* **Ethyl Bromodiethylacetylalophanate.** J. CALISEN (U.S. Pat. 1424236).—Ethyl bromodiethylacetylalophanate, $\text{C}_2\text{Et}_2\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$,

colourless crystals, m. p. $62-63^\circ$, is obtained by heating bromodiethylacetylcarbimide with urethane and crystallising the product from light petroleum.

CHEMICAL ABSTRACTS.

Preparation of Hydrocyanic Acid in Large Quantities in the Laboratory. E. FRITZMANN (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 227—234).—For preparing hydrocyanic acid from potassium ferrocyanide, sulphuric acid, and water, less of the last two ingredients than is usually recommended may be employed, the yield of the acid and the velocity of the reaction remaining unimpaired if the three reagents are taken in the proportions 10:5:8. The apparatus used is described.

T. H. P.

The X-Ray Structure of Potassium Cyanide. P. A. COOPER (*Nature*, 1922, 110, 544).—Polemical (cf. *ibid.*, 1921, 107, 745; Bozworth, this vol., i, 441).

A. A. E.

Preparation of Cyanuric Triazide. ERWIN OTT (D.R.P. 355926; from *Chem. Zentr.*, 1922, iv, 550; cf. Ott and Ohse, A., 1921, i, 231).—In the preparation of cyanuric triazide from cyanuric trihydrazide, $\text{C}_3\text{H}_9\text{N}_9$, and nitrites (Swiss Pat. 89718), the following occur as intermediate products depending on the amount of nitrite used and the duration of the reaction. *Cyanuric dihydrazidomonoazide*, $\text{C}_3\text{H}_6\text{N}_{10}$, crystalline, m. p. $85-87^\circ$; and *cyanuric monohydrazidodiazide*, $\text{C}_3\text{H}_3\text{N}_{11}$, crystalline, m. p. $87-88^\circ$. These compounds are less sensitive to percussion than the pure cyanuric triazide, C_3N_{12} .

G. W. R.

Electrolysis of Organo-magnesium Compounds. N. V. KONDYREV (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 17—24).—Experiments with magnesium ethyl bromide, magnesium propyl bromide, and magnesium phenyl bromide show that, when dissolved in dry ether, these compounds function as electrolytes. When a current is passed through the ethereal solution by means of a platinum cathode and a zinc or aluminium anode, and a copper voltameter is included in the circuit, the amount of zinc or aluminium which passes into solution corresponds exactly with the amount of copper deposited in the voltameter, aluminium behaving as a trivalent metal; a deposit of magnesium is formed at the same time on the platinum cathode. When, however, the anode consists of copper, the latter passes into solution only in traces. There is little doubt that organo-zinc and organo-aluminium compounds are formed in this way when corresponding metals are used as the anode and it may be possible to prepare these compounds by such means.

T. H. P.

Magnesium Compounds of the Olefines. I, II, and III. VL. KRETSINSKI (*Ber.*, 1922, 55, [B], 2754—2762, 2762—2770, 2770—2774; *J. Russ. Phys. Chem. Soc.*; 1920, 52, 63—74, 75—84, 85—90).—I. Alkenyl haloids in which the halogen atom is

attached to the carbon atom from which the double bond proceeds have been but little used in the formation of Grignard's reagents possibly on account of Grignard's supposition that such haloids would either not react with the metal at all or only in an abnormal manner. The only cases previously investigated appear to be the action of magnesium on α -bromostyrene and the application of vinyl haloids to the production of erythrene (Austerweil, A., 1912, i, 525). The behaviour of β -methyl- Δ^{α} -propenyl bromide (isocrotyl bromide), CMe_2CHBr , has now been investigated in a series of researches of which this communication gives the first account.

A solution of isocrotyl bromide in anhydrous ether does not react with magnesium under the usual conditions and only does so slowly and incompletely when the mixture is warmed or iodine is added. In the presence of Bacyer's pre-activated magnesium an energetic action occurs which can only be regulated with difficulty, since undue rise of temperature causes the Grignard reagent to decompose with the copious evolution of gas, whereas action soon ceases when the mixture is cooled. The course of the action can be most easily regulated when the ethereal solution of the haloid is added gradually to the mechanically-stirred mixture of the other components; it is not possible, however, to cause the whole of the magnesium to enter into reaction. The gas evolved is mainly isobutylene, which is converted by bromine into a mixture of $\alpha\beta$ -dibromoisobutane, $\text{CMe}_2\text{Br}\cdot\text{CH}_2\text{Br}$, b. p. $54-56^\circ/24$ mm., $149-151^\circ$ /normal pressure, d_4^{20} 1.7827, n_D^{20} 1.51406, n_D^{25} 1.51186, and a tribromoisobutane, b. p. $107-109^\circ/19$ mm. The course of the action is represented most simply by the schemes $\text{CMe}_2\text{CH}\cdot\text{MgBr} \rightarrow \text{CMe}_2\text{C} < [\text{or } \text{CH}_2\cdot\text{CMe}\cdot\text{CH}-] + \text{H}\cdot\text{MgBr}$ and $\text{CMe}_2\text{CHBr} + \text{H}\cdot\text{MgBr} = \text{CMe}_2\text{CH}_2 + \text{MgBr}_2$. The fate of the radicle $\text{CMe}_2\text{C} <$ or $-\text{CH}_2\cdot\text{CMe}\cdot\text{CH}-$ remains undecided. An examination of the products of the action of water on the Grignard solution only led to the isolation of ill-defined products containing oxygen.

Magnesium and isocrotyl bromide react with acetaldehyde in ethereal solution to yield ethyl alcohol, methylisocrotylcarbinol, $\text{CMe}_2\text{CH}\cdot\text{CHMe}\cdot\text{OH}$, and two fractions, b. p. $80-87^\circ/15$ mm., d_4^{20} 0.8596, n_D^{20} 1.45534, and b. p. $87-97^\circ/15$ mm., d_4^{20} 0.8763, n_D^{20} 1.45854, which appear to be a mixture of isomeric alcohols, $\text{C}_{10}\text{H}_{18}\text{O}$; a fourth fraction, b. p. $228-232^\circ$, has not been investigated further. Methylisocrotylcarbinol has b. p. $136-138^\circ$, d_4^{20} 0.8384, n_D^{20} 1.43159, n_D^{25} 1.43430, n_D^{30} 1.44098, n_D^{35} 1.44721. It is transformed by acetic anhydride at 100° into a mixture of δ -methyl- $\Delta^{\alpha\gamma}$ -pentadiene, $\text{CMe}_2\text{CH}\cdot\text{CH}\cdot\text{CH}_2$, b. p. $75.5-76^\circ$, d_4^{20} 0.72155, n_D^{20} 1.44664, and methylisocrotylcarbinyl acetate, $\text{OAc}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CMe}_2$, b. p. $140-146^\circ$.

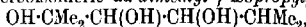
II. The action of magnesium isocrotyl bromide on isobutaldehyde has been examined.

isocrotyl bromide, magnesium, and isobutaldehyde are caused to react in the presence of ether, and the product is submitted to fractional distillation whereby isobutyl alcohol, isopropylisocrotylcarbinol, $\text{CHMe}_2\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{CMe}_2$, and fractions of higher boiling

point from which homogeneous products could not be separated are obtained. *iso*Propylisocrotylcarbinol has b. p. 161—163°, d_4^{20} 0.8444, n_D^{20} 1.44493. It is converted by acetic anhydride at 100° into *isopropylisocrotylcarbinyl acetate*, b. p. 177—180°, d_4^{20} 0.8270, n_D^{20} 1.43288, and β -*dimethyl- Δ^6 -heptadiene*,



b. p. 116—118°, d_4^{20} 0.7412, n_D^{20} 1.45024. The constitution of the hydrocarbon is deduced from its oxidation by potassium permanganate to formic, acetic, and isobutyric acids. The production of a hydrocarbon of this constitution from *isopropylisocrotylcarbinol* is difficult to explain unless it is assumed that the substance not only is acetylated by acetic anhydride, but also simultaneously unites with a molecule of acetic acid which is eliminated subsequently in a different direction, thus: $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CHMe}_2 \rightarrow \text{OAc}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CHMe}_2 \rightarrow \text{CH}_2\cdot\text{CMe}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CHMe}_2$. The constitution assigned to *isopropylisocrotylcarbinol* is established by the observation that it is oxidised by potassium permanganate to acetone, two stereoisomeric α -*dimethyl- γ -isopropylglycerols*,



sparingly soluble crystals, m. p. 159—160°, and a very hygroscopic substance, m. p. 73—75°, respectively, formic, acetic, and isobutyric acids, and a non-crystalline acid, $\text{CHMe}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$, which is analysed in the form of its calcium salt, $(\text{C}_5\text{H}_7\text{O}_3)_2\text{Ca}\cdot\text{H}_2\text{O}$, and characterised further by the formation of a crystalline *semicarbazone*. Re-examination of the action of acetic anhydride on *isopropylisocrotylcarbinol* shows that two isomeric *acetates*, $\text{C}_{10}\text{H}_{18}\text{O}_2$, are actually produced which have b. p. 167—170°, d_4^{20} 0.88676, n_D^{20} 1.43739, and b. p. 174—176°, d_4^{20} 0.88226, n_D^{20} 1.43238, respectively. When hydrolysed with barium hydroxide solution two *alcohols*, $\text{C}_8\text{H}_{16}\text{O}$, b. p. 158—161°, d_4^{20} 0.8449, n_D^{20} 1.43679, and b. p. 160—165°, d_4^{20} 0.8455, n_D^{20} 1.43789, respectively, are obtained, but on account of lack of substance it has not yet been found possible to elucidate their constitution.

*iso*Propylisocrotylcarbinol is converted by aluminium oxide at an incipient red heat mainly into diisocrotyl, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}_2$, b. p. 132—138° (which is transformed by hydrogen bromide into the hydrobromide, m. p. 65°), and (?) β -*dimethyl- Δ^6 -heptadiene*, $\text{CMe}_2\cdot\text{C}\cdot\text{CH}\cdot\text{CHMe}_2$, b. p. 119—123°, d_4^{20} 0.7637, n_D^{20} 1.45054.

III. *Phenylisocrotylcarbinol*, $\text{CMe}_2\cdot\text{CH}\cdot\text{CHPh}\cdot\text{OH}$, a colourless liquid, b. p. 122—125°/7 mm., d_4^{20} 0.9861, n_D^{20} 1.53516, is prepared by the action of magnesium isocrotyl bromide on benzaldehyde.

The observations have been extended to α -methylisocrotyl bromide [γ -bromo-3-methyl- Δ^2 -butylene], $\text{CMe}_2\cdot\text{CBrMe}$. The substance reacts with magnesium in much the same manner as, but with rather more difficulty than, its simpler homologue. Trimethylethylene [β -methyl- Δ^2 -butylene] is evolved in large quantity and is identified by converting it into dibromopentane and *tert*-amyl iodide; it appears to be the sole gaseous product of the change. Decomposition of the Grignard reagent with water leads to the further evolution of large volumes of trimethylethylene. The non-volatile products are unsaturated compounds which con-

tain oxygen; their nature has not been established definitely. The action of magnesium α -methylisocrotyl bromide on acetaldehyde appears to lead to the formation of *methyl- α , β -dimethyl- α -propenylcarbinol*, $\text{CMe}_2\text{CMeCHMeOH}$, which, however, has not been investigated closely.

The action of an ethereal solution of vinyl bromide on activated magnesium commences very rapidly and proceeds with the evolution of a mixture of acetylene and ethylene. H. W.

Derivatives of Methylstannonic Acid. Their Bearing upon its Constitution. HERBERT LAMBOURNE (T., 1922, 121, 2533—2540).

The Dinitro-derivatives of *p*-Dichlorobenzene. ANNIE LOUISE MACLEOD, MARION C. PFUND, and MARY L. KILPATRICK (*J. Amer. Chem. Soc.*, 1922, 44, 2260—2271).—The product, m. p. 81° , obtained as one of the products of nitration of *p*-dichlorobenzene (cf. Nason, A., 1919, i, 10) is shown to be a molecular compound of 2:5-dichloro-1:4-dinitro- and 2:5-dichloro-1:3-dinitro-benzene, the proportions approximating to two molecules of the former to three of the latter. When this substance was reduced by tin and hydrochloric acid a mixture of the corresponding diamines was obtained.

From a study of the action of alcoholic ammonia on the isomeric dichlorodinitrobenzenes, it is shown that the *m*-dinitro-derivative is converted entirely into chlorodinitroaniline, the chlorine atom in the ortho-position to the two nitro-groups being replaced by an amino-group. With the *o*- and *p*-dinitro-derivatives, the main reaction results in the replacement of one nitro-group by an amino-group, but at the same time a comparatively small amount of the corresponding dinitro-*p*-phenylenediamine is produced.

On reduction by tin and hydrochloric acid, 3:6-dichloro-1:2-dinitrobenzene yields 3:6-dichloro-*o*-phenylenediamine, m. p. 98° , which condensed with benzil to give 1:4-dichlorodiphenylquinazoline, m. p. 214° . W. G.

Aromatic Sulphonyl Chlorides. JESSIE STEWART (T., 1922, 121, 2555—2561).

Preparation of Aryl Sulphonic Esters of Halogenated Aliphatic Alcohols. GEORG VON KERESZTY and EMIL WOLF (D.R.-P. 353195; from *Chem. Zentr.*, 1922, iv, 156).—An arylsulphonyl chloride mixed with a halogenated aliphatic alcohol is shaken at low temperatures with concentrated alkali hydroxide solution until an alkaline reaction persists. The ester formed is rapidly hydrolysed. *Chloroethyl benzenesulphonate*, from benzenesulphonyl chloride and glycol chlorohydrin, has b. p. $184^\circ/8$ —11 mm. *Bromoethyl benzenesulphonate*, similarly prepared, has b. p. $192^\circ/20$ mm. *Dichloropropyl benzenesulphonate*, from α -dichlorohydrin and benzenesulphonyl chloride, has b. p. $205^\circ/20$ mm. and m. p. 50° . G. W. R.

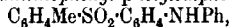
The Labile Nature of the Halogen Atom in Organic Compounds. VI. The Action of Titanous Chloride and of Ammonia on Representative Halogen Compounds. IAN ARMSTRONG BLACK, EDMUND LANGLEY HIRST, and ALEXANDER KILLEN MACBETH (T., 1922, 121, 2527—2533).

Thermal Analysis of the System o-:p-Toluenesulphonamides. A. F. DOBRJANSKI (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 139—144).—Thermal analysis of this system yields a melting-point curve composed of two branches intersecting at the eutectic point about 108°, which corresponds with 42.5% and 57.5% of the ortho- and para-isomerides, respectively. This eutectic point is identical with the melting point of the non-separable mixture of the two amides obtained in practice when the mixture of the corresponding ortho- and para-chlorides is treated with ammonia. Separation of the para-amide from this mixture by fractional precipitation should hence be, and is found experimentally to be, impossible. The acicular crystals, m. p. 120°, mentioned by Fahlberg, correspond with a mixture in equal parts of the two isomerides, but no indication is obtained of the formation of a molecular compound and no distectic point is observed; such crystals are readily resolved into their components under the microscope.

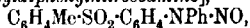
T. H. P.

Transformation of the Diphenyl-, Phenyl-p'-tolyl-, and Di-p'-tolyl-amides of Toluene-p-sulphonic Acid. J. HALBERKANN (*Ber.*, 1922, 55, [B], 3074—3095; cf. A., 1921, i, 680, 779).—In continuation of previous work, the behaviour of diarylamides of toluene-p-sulphonic acids has been investigated and transformations similar to those recorded for the mixed aromatic amides (*loc. cit.*) have been observed.

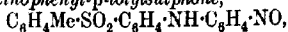
p-Toluenesulphonodiphenylamide, $C_6H_4Me \cdot SO_2 \cdot NPh_2$, m. p. 142°, prepared by heating diphenylamine with toluene-p-sulphonyl chloride in the presence of pyridine, is almost quantitatively hydrolysed when heated with sulphuric acid (*d* 1.74). Its behaviour towards concentrated sulphuric acid depends greatly on the temperature used; at 100°, sulphonation occurs to a considerable extent and the remainder of the amide is partly hydrolysed and partly isomerised. The most favourable temperature for transformation is 20°, under which conditions 75% of the amide is converted into o-anilinophenyl-p-tolylsulphone,



colourless, prismatic rods, m. p. 96—97°. The latter substance is converted by hydrochloric acid and sodium nitrite in the presence of aqueous acetone into o'-phenylnitrosoaminophenyl-p-tolylsulphone [o'-p-toluenesulphonyldiphenylnitrosoamine],



colourless crystals, m. p. 126—127°. Treatment of a concentrated ethereal solution of the nitrosoamine with a saturated solution of hydrogen chloride in ethyl alcohol brings about its isomerisation to 2-p-nitrosoanilinophenyl-p-tolylsulphone,



large, steel-blue crystals which appear green by reflected light and give a dark green powder, m. p. 150—151° [the *hydrochloride*, an ochre-coloured powder, m. p. 197° (complete decomp.) after darkening above 150°, is described], which is reduced by sodium hyposulphite in alkaline solution to 2-*p*-aminoanilinophenyl-*p*-tolylsulphone, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, colourless, prismatic crystals, m. p. 134—135°; the amine can be diazotised and then couples normally with β -naphthol to yield *p*-toluenesulphonyl-*o*'-anilino-*p*'-benzeneazo- β -naphthol,

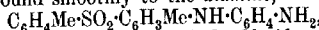
$\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, small, red needles, m. p. 172°. 2-*p*-Nitrosoanilinophenyl-*p*-tolylsulphone is converted by protracted treatment with aqueous sodium hydroxide solution into *o*'-aminophenyl-*p*-tolylsulphone, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, colourless, prismatic rods which readily become red, m. p. 120—121°, which is diazotised and coupled with β -naphthol to form *p*-toluenesulphonylbenzeneazo- β -naphthol,

$\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, brownish-red, lustrous needles, m. p. 208°.

The proof that the amino-group in aminophenyl-*p*-tolylsulphone, m. p. 120—121°, occupies the ortho-position is obtained in two ways. On the one hand, *p*'-aminophenyl-*p*-tolylsulphone, groups of colourless, four-sided rods, m. p. 181°, is synthesised from *N*-acetyl-*p*-sulphanilic chloride and toluene by the Friedel-Crafts' reaction and subsequent hydrolysis of the product with hydrochloric acid. On the other, if wandering normally occurs towards the ortho-position even when the para-position is free, the compound m. p. 120—121° should be obtainable in the following manner (this is the case). *p*-Toluenesulphonanilide is quantitatively transformed by ethyl toluene-*p*-sulphonate or ethyl sulphate into the corresponding *N*-ethyl compound, m. p. 87—88°, which is partly hydrolysed and partly isomerised by concentrated sulphuric acid to *o*'-ethylaminophenyl-*p*-tolylsulphone, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHEt}$, coarse, colourless prisms, m. p. 90—91° [acetyl derivative, hexagonal needles or plates, m. p. 141° (cf. Witt, A., 1913, i, 360)]. De-ethylation of the compounds is effected with considerable difficulty by heating it at 270—275° in a current of dry hydrogen chloride. The small amount of *o*'-aminophenyl-*p*-tolylsulphone which is produced is isolated by diazotising the crude product, coupling the diazo-solution with resorcinol, filtering the solution, precipitating the dye by addition of acid, and subsequently reducing it to the amine by means of sodium hyposulphite. The product has m. p. 120°.

Toluene-p-sulphonphenyl-*p*'-tolylamide, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NPh}\cdot\text{C}_6\text{H}_4\text{Me}$, colourless, four-sided needles, m. p. 122—123°, is prepared by heating toluene-*p*-sulphonyl chloride with phenyl-*p*-tolylamine in the presence of pyridine. It is converted by concentrated sulphuric acid into a mixture of the two possible sulphones, the reaction being accompanied by very little hydrolysis. 2-*p*-Toluidinophenyl-*p*-tolylsulphone, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, almost colourless, coarse prisms or four-sided prismatic rods, m. p. 147°, is readily isolated from the product by reason of its sparing solubility in

alcohol. It gives an *N*-acetyl derivative, colourless, prismatic rods, m. p. 164—165°, and an *N*-nitroso-compound, aggregates of pale yellow needles, m. p. 168° (decomp.); the latter regenerates the parent compound when treated with hydrogen chloride in the presence of alcohol and ether and does not become isomerised to the nuclear nitroso-compound although the para-position in the benzene nucleus is not occupied. The second sulphone is isolated by converting the mixture obtained as above into the corresponding nitroso-derivatives, which are separated mechanically from one another and subsequently reduced by phenylhydrazine. *p*-Tolyl-1-anilino-*m*-tolylsulphone, $C_6H_4Me \cdot SO_2 \cdot C_6H_3Me \cdot NHPh$, forms coarse, colourless crystals, m. p. 124°. The corresponding nitrosoamine crystallises in brown, hexagonal plates or large rhombs, m. p. 132° (decomp.); it is reduced by zinc dust and acetic acid in the presence of acetone and alcohol to the corresponding hydrazine, $C_{20}H_{20}O_2N_2S$, coarse, colourless prisms, m. p. 169—170° (benzylidene compound, $C_{27}H_{24}O_2N_2S$, pale yellow prisms, m. p. 195°). The nitrosoamine is isomerised by hydrogen chloride in the presence of alcohol and ether to the corresponding *p*-nitrosophenyl compound, $C_6H_4Me \cdot SO_2 \cdot C_6H_3Me \cdot NH \cdot C_6H_4NO$, greenish-yellow, prismatic needles, m. p. 174—175° (apparent decomp.) [the hydrochloride, brownish-red prisms, m. p. 178—179° (decomp.) after darkening at about 160° is described]. Ammonium sulphide reduces the *p*-nitroso-compound smoothly to the diamine,



colourless crystals, m. p. 148—149° (hydrochloride, colourless needles or plates), whereas with sodium hyposulphite or zinc dust as reducing agent an azo-compound, $C_{20}H_{16}O_4N_4S_2$, m. p. 267—268°, is also formed (the latter is produced also by heating molecular quantities of the *p*-nitroso- and *p*-amino-compounds dissolved in glacial acetic acid). When heated with sodium hydroxide solution (10%) at 140°, the *p*-nitroso-compound is converted into *p*-tolyl-6-amino-*m*-tolylsulphone, $C_6H_4Me \cdot SO_2 \cdot C_6H_3Me \cdot NH_2$, m. p. 168—169°. The transformation of toluene-*p*-sulphonphenyl-*p*'-tolylamide is always accompanied by a greater or less amount of sulphonation. The free sulphonic acid, $C_6H_4Me \cdot SO_2 \cdot C_6H_3Me \cdot NH \cdot C_6H_4 \cdot SO_3H$, crystallises in colourless, slender needles (+2H₂O), m. p. 146° (decomp.); the corresponding barium salt has m. p. 269—270° (a mono- and a di-hydrate are described).

Toluene-*p*-sulphon-di-*p*-tolylamide, $C_6H_4Me \cdot SO_2 \cdot N(C_6H_4Me)_2$, colourless, rhombic plates, m. p. 144°, is isomerised quantitatively by concentrated sulphuric acid at 60° into the corresponding sulphone, $C_6H_4Me \cdot SO_2 \cdot C_6H_3Me \cdot NH \cdot C_6H_4Me$, long, colourless needles, m. p. 110—111°. The latter yields an *N*-nitroso-derivative, $C_{21}H_{20}O_2N_2S$, pale yellow, hexagonal platelets, m. p. 148—149°, which is reconverted into the sulphone when treated with hydrogen chloride in the presence of alcohol and ether.

H. W.

Union of Hydrogen with Acetylene Derivatives. XIV.
Hydrogenation of Phenylacetylene. J. S. ZALKIND (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 191—198).—The velocity of hydro-

genation of phenylacetylene in presence of colloidal platinum increases to a maximum after combination of the first two atoms of hydrogen and subsequently diminishes. The reaction proceeds, but extremely slowly, after four atoms of hydrogen have been combined; characteristic of this late stage of the hydrogenation is the fact that it proceeds more rapidly with low than with high concentrations of the catalyst. Further, hydrogenation of the triple to the double linking takes place more slowly than that of the double to the single linking.

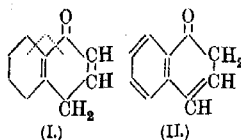
The results of experiments with styrene indicate that, in the nascent state, this compound is more readily hydrogenated than when ready-formed. Here, too, the hydrogenation does not cease when the side-chain is converted into the ethyl group, but is continued at the expense of the double linkings of the nucleus. It seems possible, indeed, that the initial stage of the reaction proceeds in two different directions, yielding, not merely ethylbenzene, but also 5-methyl- $\Delta^{1,2}$ -cyclohexadiene.

T. H. P.

The Action of Bromine Water on Indene. JOHN READ and ERIC HURST (T., 1922, 121, 2550—2554).

Chemistry of Naphthalene and its Derivatives : Chemical Peculiarities of the Naphthalene Nucleus. N. N. VOROSHOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, 6, 125—151).—The author discusses the four principal structural formulæ which have been proposed for the naphthalene molecule: (1) That proposed by Erlenmeyer (*Annalen*, 1866, 137, 346) and Graebe (*Ber.*, 1868, 1, 36) and expounded by Marekwald (A., 1894, i, 474; 1895, i, 244) and composed of two benzene rings having two common carbon atoms; (2) Bamberger's formula (A., 1890, 1299); (3) Thiele's formula (A., 1899, i, 534), and (4) the formula proposed by Harries (A., 1906, i, 225) and Willstätter and King (A., 1913, i, 353). The identity of the two six-membered rings in naphthalene appears certain, in the absence of evidence that isomeric mono-substituted naphthalenes exist with the substituents in the same position. Besides being unsymmetrical, Willstätter's formula rests on inadequate foundations. Thiele's formula appears the most probable, as it brings out the special reactivity of the α -position. The different behaviour shown towards reagents by benzene and by octatetrene cannot be advanced as an argument against Thiele's theory, as it may be explained by differences between six- and eight-membered rings.

In the monohydroxy- and monoamino-derivatives of naphthalene, however, the naphthalene nucleus exhibits other relations. The results of the author's investigations on the action of sodium hydrogen sulphite on naphthalene derivatives (A., 1916, i, 293) do not agree with Bucherer's statements (A., 1904, i, 309; 1905, i, 48), and show that the naphthols are not esterified by sulphurous acid or sulphites, but first yield additive compounds, which are regarded as formed from the ketones isomeric with the naphthols. In view of the marked analogy in reaction relationships between



the hydrogen atom in the 4-position of α -naphthol and that in the 1-position of β -naphthol, the constitution I is favoured for the keto-form of α -naphthol, although the structure II is not excluded. Thiele's theory of conjugated double linkings renders it probable that the keto-forms of the

naphthols are but slightly unsaturated.

The divergent behaviour shown by benzene and naphthalene derivatives evidenced in the alkylation of the naphthols in acid solution, in the amination of the hydroxy-group and hydrolysis of the amino-group, and in the reaction with sulphites, is readily explainable on the assumption that the hydroxy- and amino-derivatives of the naphthalene series more readily undergo keto-enolic transformations than the corresponding compounds of the benzene series. Thus, hydroxy-derivatives of naphthalene are true enols, whereas the hydroxyl of the monohydroxyl derivatives of the benzene series functions as aromatically combined hydroxyl; this conclusion is not in accord with the views of Meyer (A., 1913, i, 704), but is supported by various reactions of naphthalene derivatives. Application of the sulphite reaction to the naphthylene-1:5- and -1:8-diamines results in the formation of the additive compound first in one of the substituted rings, the second ring remaining intact as a typically aromatic ring. If then the sulphurous acid additive compound is destroyed, the amino-group of the second ring reacts on subsequent treatment with sulphurous acid; in this case the second ring exhibits aliphatically-unsaturated, and the first aromatic behaviour. The various stages of the reaction are in agreement with the author's views. T. H. P.

Preparation of Symmetrical Octahydroanthracenes. GEORG SCHROETER and TETRALIN G. M. B. H. (D.R.P. 352721; from *Chem. Zentr.*, 1922, iv, 159).—Purified anthracene, melted or in solution, is treated with hydrogen under pressure in the presence of catalysts. For example, purified anthracene, m. p. 214°, is dissolved in tetrahydronaphthalene and in the presence of a catalyst, prepared by precipitation of reduced nickel on fuller's earth, treated with hydrogen at 180–200° under a pressure of 10–15 atmospheres until a quantity equivalent to four molecules is absorbed. The product is fractionated under reduced pressure.

s-Octahydroanthracene, $C_6H_8 \begin{smallmatrix} <CH> \\ <CH> \end{smallmatrix} C_6H_8$, forms crystals, m. p. 72–73°, b. p. 160–162°/11 mm. It forms a monosulphonic acid, $C_6H_8 \begin{smallmatrix} <CH> \\ <C(SO_3H)> \end{smallmatrix} C_6H_8$. With chlorine and bromine crystalline halogen substitution products are formed. By oxidation with chromium trioxide, 4-keto-*s*-octahydroanthracene is obtained. The symmetrical constitution of the octahydroanthracene is shown by the following synthesis. Tetrahydronaphthalene gives with chloroacetyl chloride in the presence of phosphoric oxide α - and β -tetra-

hydronaphthoylacetyl chlorides, $C_{10}H_{11} \cdot CO \cdot CH_2 \cdot COCl$; the latter give with ethyl sodiomalonate *ethyl* α - and β -*tetrahydronaphthoylacetymalonates*, $C_{10}H_{11} \cdot CO \cdot CH_2 \cdot CH(CO_2Et)_2$, which by hydrolysis give α - and β -*tetrahydronaphthoylpropionic acids*,
 $C_{10}H_{11} \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$.

By reduction, these acids yield α - and β -*tetrahydronaphthylbutyric acids*. From the chlorides of these acids cyclic ketones are obtained by inner condensation. From β -*tetrahydronaphthylbutyryl chloride*, 4-keto-*s*-octahydroanthracene and 4-keto-*s*-octahydrophenanthrene are obtained and may be separated by means of their *semicarbazones*. 4-Keto-*s*-octahydroanthracene yields, on reduction, *s*-octahydroanthracene, m. p. 72–73°, identical with that prepared by the catalytic process. Similarly, catalytic *s*-octahydroanthracene gives on oxidation with chromium trioxide 4-keto-*s*-octahydroanthracene identical with the compound obtained in the above synthesis.

G. W. R.

Preparation of Symmetrical Octahydrophenanthrenes. GEORG SCHROETER and TETRALIN G. M. B. H. (D.R.-P. 352719; from *Chem. Zentr.*, 1922, iv, 159–160).—Purified phenanthrene, melted or in solution, is hydrogenated in the presence of catalysts. For example, phenanthrene, purified by treatment with readily fusible or finely divided metals such as sodium, potassium, copper, iron, or nickel, or other metallic compounds such as sodamide or calcium carbide, is treated with hydrogen at 180–220° at 15 atmospheres pressure in the presence of a catalyst prepared by precipitating nickel on fuller's earth. The product, b. p. 160–170°/13 mm., is purified by way of its *sulphonic acid* (I) which by treatment with hydrochloric acid
 (I) $\begin{array}{c} C_6H_8 \cdot C \cdot SO_3H \\ | \\ C_6H_8 \cdot CH \end{array}$ (II) $\begin{array}{c} C_6H_8 \cdot CH \\ | \\ C_6H_8 \cdot CH \end{array}$ gives *s*-octahydrophenanthrene (II). The latter compound forms crystals, m. p. 16–7°, b. p. 167–5°/13 mm., d_{20}^{20} 1.026. Its constitution is demonstrated in the same way as that of the *s*-octahydroanthracene (see preceding abstract). *s*-Octahydrophenanthrenemono-sulphonic acid gives a stable *chloride* which with dilute aniline solution yields a crystalline *anilide*.

G. W. R.

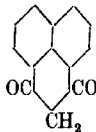
Diphenylene-ethylene. HEINRICH WIELAND, FRITZ REINDEL, and JUAN FERRER (*Ber.*, 1922, 55, [B], 3313–3317).—The preparation of diphenylene-ethylene [dibenzofulvene], $\begin{array}{c} C_6H_4 \\ \diagup \quad \diagdown \\ C_6H_4 \end{array} > C \cdot CH_2$,

by leading the vapours of fluorene over heated lead oxide has been described by Manchot and Kriche (A., 1905, i, 142) and by Sieglitz and Jassoy (A., 1921, i, 791); repetition of their work shows that the product is a mixture of fluorene and bidiphenylene-ethylene. For the preparation of the hydrocarbon, 9-methyl-fluorenol (Daufresne, A., 1908, i, 164) is mixed with dry aluminium phosphate and distilled under diminished pressure; the monomeric substance is obtained in only very small yield on account of the unusual readiness with which it polymerises at a high temperature. The isolated polymeride can be depolymerised by a second heating, but the isolation of the monomeride is not possible even by dis-

tillation in a high vacuum. The product is therefore converted into the crystalline *dibromide*, broad, lustrous needles, m. p. 143° (decomp.), which is debrominated by treating its solution in alcohol with zinc dust and acetic acid; the operation must be performed in artificial light. *Diphenylene-ethylene* crystallises in lustrous, pointed prisms, m. p. 53°. It may be preserved unchanged for a few hours if shielded from daylight, but is rapidly polymerised when exposed even to diffused daylight or the rays from a mercury lamp. In solution, it is considerably more stable; thus, the ethereal solution is unchanged after being illuminated during twenty minutes by the mercury lamp. Polymerisation is not accelerated by ethereal hydrogen chloride. It instantly combines with bromine with re-formation of the dibromide. It is readily reduced by hydrogen in ethereal solution in the presence of palladium black to 9-methylfluorene, m. p. 45–46°. The *polymeride*, $(C_{14}H_{10})_n$, is a chalky, amorphous, colourless powder, which commences to soften at about 270°, whereby incipient depolymerisation begins. H. W.

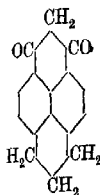
Synthesis of Pyrene. KARL FLEISCHER and EWALD RETZE (*Ber.*, 1922, 55, [B], 3280–3290).—A direct synthesis of pyrene from naphthalene has been effected by condensing the latter with malonyl bromide, reducing the product, again condensing the reduction product with malonyl bromide, and submitting the compound so produced to a final reduction.

A solution of malonyl bromide and naphthalene in carbon disulphide is converted by aluminium chloride into *peri*-naphthindanedione (annexed formula), decomp. about 265° after darkening at 250°, which is identical with the product obtained by Errera (A., 1911, i, 465) by the action of naphthalic anhydride on ethyl malonate in the presence of zinc chloride; malonyl chloride may be substituted for the bromide with equally good results. A suspension of the dione in benzene is converted by phosphorus pentachloride into 3 : 3-dichloro-1-ketoperinaphthindane, red-



dish-brown crystals, m. p. about 340° (decomp.). Reduction of the dione to the corresponding hydrocarbon can be effected only with great difficulty. It is either not affected or converted into amorphous products, which retain the property of solubility in alkali hydroxide, by amalgamated zinc and hydrochloric acid, zinc or magnesium, and glacial acetic acid, zinc dust in alkaline solution, sodium amalgam, sodium and amyl alcohol or cyclohexanol. Treatment with hydriodic acid (*d* 1.7) and red phosphorus under pressure converts the keto- into methylene groups, but the product also suffers hydrogenation in the nucleus; since the conditions of the reaction cannot be precisely governed, a mixture of hydrogenated hydrocarbons is produced. The product can, however, be dehydrogenated by passage over freshly-reduced copper at 500° thereby yielding *peritrimethylenenaphthalene* (*perinaphthindane*), m. p. 68–69°, identical with the product isolated by Langstein (A., 1910, i, 726) by the degradation of pyrene. It is very sensitive towards air. The corresponding *picrate* crystallises

in red needles, m. p. 134–135° after becoming discoloured at 124°, whereas the additive compound with 1:3:5-trinitrobenzene forms yellow needles, m. p. 159–160° after becoming discoloured at 130°.



*peri*Naphthindane reacts with malonyl bromide in the presence of carbon disulphide and aluminium chloride to give 1:3-diketo-1:2:3:4:5:6-hexahydropyrene (annexed formula), a pale yellow, amorphous substance which does not melt below 280°. It is converted by distillation with zinc dust in a slow current of hydrogen into pyrene, the identity of which is established by converting it into the picrate, long, red needles, m. p. 215°.

H. W.

Amine Oxidation. VI. Radicles as Intermediate Stages in Chemical Reactions. STEFAN GOLDSCHMIDT and BERNARD WURZSCHMITT (*Ber.*, 1922, 55, [B], 3216–3220).—A characteristic property of organic radicles is their ability to combine with the radicles of other elements to form relatively stable additive compounds. This behaviour may be used in the detection of the transitory existence of radicles during the course of a chemical reaction provided that the second radicle is not itself changed under the experimental conditions used, and that the velocity of addition of the radicles is greater than that of the polymerisation of the intermediate radicle. From this point of view, the oxidation of aniline, *p*-toluidine, and *o*-toluidine dissolved in ether by lead peroxide in the presence of ignited sodium sulphate and hexaphenylethane has been investigated; anilinetriphenylmethane, colourless, hexagonal prisms, m. p. 148–149°, *p*-toluidinetriphenylmethane, m. p. 176°, and *o*-toluidinetriphenylmethane, m. p. 142°, respectively, are thereby obtained in good yield, thus showing that the radicle $R\cdot NH_2$ is intermediately produced (which probably becomes transformed into $R\cdot N$ and $R\cdot NH_2$). Under similar conditions, diphenylamine yields solely tetraphenylhydrazine; diphenylaminotriphenylmethane cannot be obtained even by considerable variation of the experimental conditions. The rate of polymerisation of diphenylnitrogen appears to be much greater than its velocity of combination with triphenylmethyl.

The thermal decomposition of hydrazobenzene into azobenzene and aniline has been interpreted by Stieglitz and Curme (*A.*, 1913, ii, 398) as taking place in accordance with the scheme: $NHPh\cdot NHPh \rightarrow PhN\cdot + PhNH_2$, whereas Wieland (1915, i, 850) has considered it to occur thus: $NHPh\cdot NHPh = NPh\cdot NPh + 2H$. Conclusive evidence in favour of the latter view is deduced from the observation that azobenzene and triphenylmethane are almost quantitatively produced when a solution of hydrazobenzene in toluene is boiled with triphenylmethyl in an atmosphere of carbon dioxide; the radicle thus acts as acceptor of the activated hydrogen.

H. W.

Amine Oxidation. VII. The Oxidation of Aniline. STEFAN GOLDSCHMIDT and BERNHARD WURZSCHMITT (*Ber.*, 1922, 55, [B], 3220–3227; cf. *A.*, 1920, i, 226).—It has been suggested

previously that the formation of the different complex products of the oxidation of aniline may be due to the intermediate formation of benzoquinonephenyldi-imine or to the production and subsequent polymerisation of the radicle $\text{PhN}\cdot$. It is now found that it is explicable by the great reactivity of the former, which finds its expression in very differing directions. The second suggestion is therefore considered to be less probable and is relegated to the background.

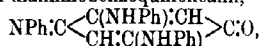
Benzoquinonephenyldi-imine is polymerised by glacial acetic or a small quantity of hydrochloric acid in the presence of ether almost quantitatively to the trimeride, $\text{NPh}\cdot\text{C}_6\text{H}_4(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NPh})_2\cdot\text{NH}$ (cf. Willstätter and Kubli, A., 1909, i, 976). It depends essentially on the nature and quantity of the added acid whether the di-imine is polymerised to emeraldine or to Willstätter's compound.

The oxidation of solutions of aniline salts by lead peroxide (cf. Börnstein, A., 1901, i, 375; Majima and Aoki, A., 1911, i, 216, 992) leads to the formation of the compound $\text{NPh}\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{C}(\text{NHPh}) \\ \text{C}(\text{NHPh})\cdot\text{CH} \end{smallmatrix}\text{C}\cdot\text{NH}$

or $\text{NPh}\cdot\text{C}\begin{smallmatrix} \text{C}(\text{NPh})\text{---CH} \\ \text{CH}\cdot\text{C}(\text{NHPh}) \end{smallmatrix}\text{C}\cdot\text{NH}_2$. It is found that benzoquinonephenyldi-imine reacts readily with aniline to form this substance under the conditions selected by Börnstein, and that, in addition, Willstätter's trimeride is produced; the latter is not isolated in the oxidative experiments, since it undergoes further change.

According to Börnstein, azophenine, $\text{NPh}\cdot\text{C}\begin{smallmatrix} \text{C}(\text{NHPh})\cdot\text{CH} \\ \text{CH}\cdot\text{C}(\text{NHPh}) \end{smallmatrix}\text{C}\cdot\text{NPh}$, is a further product of the oxidation of aniline; it is obtained when aniline is mixed with dianilinobenzoquinonephenyldi-imine in ethereal solution in the presence of a little glacial acetic acid.

The formation of dianilinobenzoquinoneanil,

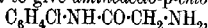


by the oxidation of aniline in acetic acid solution by hydrogen peroxide has been observed by Schunk and Marchlewski. Since benzoquinonephenyldi-imine is readily hydrolysed with loss of ammonia to benzoquinonephenylimine, $\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}$, it appears probable that the anil is produced by condensation of this substance with aniline in dilute acid solution. Such condensation is shown to take place readily and at the atmospheric temperature in ethereal solution in the presence of a little acetic acid. A second possible mode for its formation consists in the hydrolysis of Börnstein's anil; dianilinobenzoquinoneanil is actually formed from this compound by the prolonged action of dilute hydrochloric acid, but not by acetic acid, so that its preparation in this manner during oxidative experiments in dilute acetic acid solution appears improbable.

H. W.

Formation and Properties of Dithioketones ($\text{R}_2\text{C}\cdot\text{S}\cdot\text{S}$) and Dithio-ethers ($\text{R}_2\text{S}\cdot\text{S}$). III. KUMRAJI GOSAI NAIK and MAHADEO DATTATRAYA AVASARE (T., 1922, 121, 2592—2595).

Thiocyanates and Thiocarbimides. XV. The Nature of the Intramolecular Rearrangement of Thiocarbimidoacetanilides. ARTHUR J. HILL and ERWIN B. KELSEY (*J. Amer. Chem. Soc.*, 1922, 44, 2357—2369; cf. A., 1920, i, 681; Beckurts and Frerichs, A., 1915, i, 798, 799).—Using the method previously described (*loc. cit.*), the authors have converted the chloroanilides used by Beckurts and Frerichs (*loc. cit.*) successively into the corresponding primary amines, dithiocarbamates, carbethoxy-dithiocarbamates, and finally the thiocarbimides. The latter are so unstable that they rearrange immediately into normal 2-thiohydantoin. That these were normal thiohydantoin was shown by their conversion into the corresponding oxyhydantoin, which latter were also synthesised from the urethanes of the general formula $\text{NHR}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$. Further, it is shown that their melting points differ from those of the ψ -hydantoin described by Beckurts and Frerichs. Chloroaceto-*p*-chloroanilide reacts with alcoholic ammonia to give aminoaceto-*p*-chloroanilide,



m. p. 64°; and the di-*p*-chlorophenylamide of diglycolamidic acid, $(\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2)_2\text{NH}$, m. p. 170—171°, according to the conditions. The first-named anilide by the action of ethyl chloroformate is converted into the carbethoxy-derivative, m. p. 198°, and by the action of benzoyl chloride into benzoylaminoaceto-*p*-chloroanilide, m. p. 217—218°. Aminoaceto-*p*-chloroanilide reacts with carbon disulphide in alcoholic solution to give its dithiocarbamate, m. p. 155°, and the carbethoxy-derivative gives a dithiocarbamate which is unstable and on distillation is converted into 2-thio-1-*p*-chlorophenylhydantoin, m. p. 225—227° (decomp.), which is also prepared by the action of mercuric chloride on aminoaceto-*p*-chloroanilide dithiocarbamate. This hydantoin gives 2-thio-1-*p*-chlorophenyl-4-benzylidenehydantoin, m. p. 257°, and 2-benzylthiol-1-*p*-chlorophenyl-4-benzylidenehydantoin, m. p. 176.5°. 1-*p*-Chlorophenylhydantoin, m. p. 174°, was obtained either by the action of chloroacetic acid on the corresponding thiohydantoin or by the action of alcoholic potassium hydroxide on carbethoxyaminoaceto-*p*-chloroanilide and yielded 1-*p*-chlorophenyl-4-benzylidenehydantoin, m. p. 274°.

A similar series of compounds has been prepared from chloroaceto-*p*-aniside and from chloroaceto-*m*-toluidide, as follows. Aminoaceto-*p*-aniside, m. p. 98—99°; the di-*p*-anisylamide of diglycolamidic acid, m. p. 143°; the tri-*p*-anisylamide of triglycolamidic acid, m. p. 192—193°; carbethoxyaminoaceto-*p*-aniside, m. p. 154°; aminoaceto-*p*-aniside dithiocarbamate, m. p. 140—145° (decomp.), and its carbethoxy-derivative; 2-thio-1-*p*-anisylhydantoin, m. p. 207—209°; 1-*p*-anisylhydantoin, m. p. 208°; 2-thio-1-*p*-anisyl-4-benzylidenehydantoin, m. p. 203°; 2-benzylthiol-1-*p*-anisyl-4-benzylidenehydantoin, m. p. 174°; 1-*p*-anisyl-4-benzylidenehydantoin, m. p. 238°.

Aminoaceto-*m*-toluidide, m. p. 54—55°; the di-*m*-tolylamide of diglycolamidic acid, m. p. 136°; benzoylaminoaceto-*m*-toluidide, m. p. 186°; carbethoxyaminoaceto-*m*-toluidide, m. p. 103°; aminoaceto-*m*-

toluidide dithiocarbamate, m. p. 138° (decomp.), and its *carbethoxy-derivative*, m. p. 113° (decomp.); *2-thio-1-m-tolylhydantoin*, m. p. 187° (decomp.); *1-m-tolylhydantoin*, m. p. 123°; *2-thio-1-m-tolyl-4-benzylidenehydantoin*, m. p. 183°; *2-benzylthiol-1-m-tolyl-4-benzylidenehydantoin*, m. p. 145°; *1-m-tolyl-4-benzylidenehydantoin*, m. p. 214°.

The di-*p*-chlorophenylamide of diglycolamidic acid when warmed in acetone solution deposits a crystalline compound, m. p. 250–251°, which is apparently produced by the combination of two mol. of the secondary amine and one mol. of acetone. The diphenylamide of diglycolamidic acid gave a similar compound, m. p. 166–167°.

W. G.

The Mobility of Symmetrical Triad Systems. I. The Conditions Relating to Systems Terminated by Phenyl Groups. CHRISTOPHER KELK INGOLD and HENRY ALFRED PIGGOTT (T., 1922, 121, 2381–2389).

5-Aminoacenaphthene. KARL FLEISCHER and KARL SCHRANZ (Ber., 1922, 55, [B], 3253–3280).—An account is given of an extensive series of derivatives of 5-aminoacenaphthene.

Reduction of 5-aminoacenaphthene in aqueous alcoholic solution by means of sodium hyposulphite leads to the formation of a mixture of 5-aminoacenaphthene, m. p. 108° (20%), *sodium acenaphthylsulphamate*, $C_{12}H_9NH \cdot SO_3Na$ (about 50%), and 5-aminoacenaphthene-4-sulphonic acid, colourless needles which darken without melting at 270° (4%). The production of the sulphamate appears to take place in accordance with the equations: $C_{12}H_9 \cdot NO_2 + 2Na_2S_2O_4 + 3H_2O = C_{12}H_9 \cdot NH \cdot OH + 4NaHSO_3$ and $C_{12}H_9 \cdot NH \cdot OH + H \cdot SO_3Na = C_{12}H_9 \cdot NH \cdot SO_3Na + H_2O$. It forms aggregates of colourless crystals, decomp. above 235° after darkening at 200°. *Acenaphthyl-5-sulphamic acid*, $C_{12}H_9 \cdot NH \cdot SO_3H$, crystallises in slender, colourless needles, which do not melt below 270°; it is hydrolysed by boiling hydrochloric acid to 5-aminoacenaphthene and sulphuric acid. For the preparation of 5-aminoacenaphthene by the reduction of the 5-nitro-compound the procedure of Sachs and Mosebach (A., 1910, i, 726; 1911, i, 966) is modified in that the crude product of the reaction after removal of alcohol is boiled with hydrochloric acid and the base is subsequently liberated by addition of ammonia to the solution; the yield is 71% of that theoretically possible.

5-Aminoacenaphthene is converted by concentrated sulphuric acid at 100° into a mixture of di- and tri-sulphonic acids; a more dilute acid (80%), under similar conditions, converts it into 5-aminoacenaphthene-(?)6-sulphonic acid, almost colourless needles (the product is frequently amorphous) which become blackened, without melting, at 300°. It couples with diazotised *m*-nitroaniline to yield the compound, $NH_2 \cdot C_{10}H_7(SO_3Na) \cdot N \cdot N \cdot C_6H_4 \cdot NO_2$, a brownish-red powder with a metallic lustre. It is conveniently diazotised by the addition of hydrochloric acid to an aqueous solution of its sodium salt and sodium nitrite, and the dark green

diazonium compound couples with β -naphthol to the dye, $\text{SO}_3\text{Na}\cdot\text{C}_{12}\text{H}_9\text{N}\cdot\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, a brownish-red, metallic powder.

5-Aminoacenaphthene reacts with aldehydes in boiling alcoholic solution to give normal azomethines, of which the following are described: 5-benzylideneaminoacenaphthene, $\text{C}_{12}\text{H}_9\text{N}\cdot\text{CHPh}$, pale yellow plates, m. p. 67–68°; 5-o-nitrobenzylideneaminoacenaphthene, oblique, brownish-yellow prisms, m. p. 135°; 5-m-nitrobenzylideneaminoacenaphthene, lemon-yellow needles, m. p. 156° after softening at 147°; 3-p-nitrobenzylideneaminoacenaphthene, cinnabar-red prisms, m. p. 226°; 5-o-chlorobenzylideneaminoacenaphthene, yellow needles, m. p. 112–114°; 5-p-chlorobenzylideneaminoacenaphthene, yellow, rectangular plates, m. p. 126–128°; 5-o-hydroxybenzylideneaminoacenaphthene, ochre-yellow, rectangular platelets, m. p. 92–93°; 5-p-hydroxybenzylideneaminoacenaphthene, yellow, rhombic platelets, m. p. 194–196°; 5-p-methoxybenzylideneaminoacenaphthene, yellow, oblique prisms, m. p. 85–86°; 5-3':4'-dimethoxy-2'-styrylbenzylideneaminoacenaphthene, $\text{C}_{12}\text{H}_9\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4(\text{OMe})_2\cdot\text{CH}\cdot\text{CHPh}$, slender, pale yellow needles, m. p. 132–134°; 5- α -furylideneaminoacenaphthene, minute, brownish-yellow crystals, m. p. 106–108°.

The condensation of 5-aminoacenaphthene with the chlorides of dibasic acids gives symmetrical diacenaphthyl derivatives of the acid amides. The following are described: di-5-acenaphthylcarbamide, $\text{CO}(\text{NH}\cdot\text{C}_{12}\text{H}_9)_2$, slender, pale brown rods, m. p. 301° (decomp.) after darkening at 295°, prepared from the amine and carbonyl chloride in the presence of benzene; oxalodi-5-acenaphthylamide, colourless, slender rodlets, m. p. 274–275° after previous darkening; malonodi-5-acenaphthylamide, pale brown, rectangular plates, m. p. 222–223° after slight previous softening; diethylmalonodi-5-acenaphthylamide, $\text{C}_2\text{Et}_2(\text{CO}\cdot\text{NH}\cdot\text{C}_{12}\text{H}_9)_2$, slender, colourless needles, m. p. 218–220°; succinodi-5-acenaphthylamide, needles, m. p. 288–289° after previous darkening.

5-Dimethylaminoacenaphthene is conveniently prepared by the action of methyl sulphate on 5-aminoacenaphthene in the presence of concentrated aqueous sodium acetate solution and removal of simultaneously formed monomethyl derivatives by treatment of the crude product of the reaction with benzenesulphonyl chloride: it crystallises in colourless, rhombic platelets, m. p. 45–46°. It gives a picrate, canary-yellow crystals, m. p. 172–174°, and a stable methiodide, long, colourless needles, m. p. 177°; it could not be caused to react with ethyl bromide. 5-Diethylaminoacenaphthene, colourless leaflets, m. p. 41–42°, is prepared similarly by the use of ethyl sulphate. The corresponding picrate, lemon-yellow crystals, m. p. 181–184° after previous softening (decomp. 186°), and the unstable methiodide, m. p. 165–167° (decomp.), are described. The base is not affected by ethyl bromide at 100°.

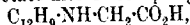
5-Aminoacenaphthene exhibits a marked tendency to form diacyl derivatives under conditions which in general lead only to the production of the mono-compounds. Thus, with benzenesulphonyl chloride in the presence of potassium hydroxide solution it gives a mixture of 5-benzenesulphonylaminoacenaphthene, colourless, rhombic platelets, m. p. 198–199° after darkening at 195°,

and 5-dibenzenesulphonylaminoacenaphthene, aggregates of colourless prisms, m. p. 220° after previous darkening. The latter substance is unaffected by concentrated, aqueous solutions of alkali hydroxides, but is converted by sodium ethoxide, dissolved in alcohol into the monobenzenesulphonyl compound. Similarly, toluene-*p*-sulphonyl chloride yields a mixture of 5-toluene-*p*-sulphonylaminoacenaphthene, pale yellow rodlets, m. p. 194–195°, and 5-ditoluene-*p*-sulphonylaminoacenaphthene, small, colourless pyramids, m. p. 215–217°, to a dark liquid. 5-Acetylmethylaminoacenaphthene has m. p. 124–125°.

The phenylation of the base could not be accomplished smoothly by treatment of it with bromobenzene and copper powder. On the other hand, it reacts with chloro-2:4-dinitrobenzene in boiling alcoholic solution to give 5-2':4'-dinitroanilinoacenaphthene, cinnamon-red needles, m. p. 177–178°, after previous softening and with picryl chloride to yield 5-2':4':6'-trinitroanilinoacenaphthene, dark red needles which soften at 230° and decompose at a higher temperature.

A diazotised solution of 5-aminoacenaphthene couples with sodium β-naphthol-3:6-disulphonate with the formation of a reddish-violet dye and with sodium α-naphthol-4-sulphonate to yield an unstable compound. Reddish-violet dyes are also obtained from diazotised 5-aminoacenaphthene-6(?)-sulphonic acid and *R*-salt or sodium α-naphthol-4-sulphonate, but the shades are not sufficiently pure to render them technically valuable.

5-Aminoacenaphthene is converted by chloroacetic acid in the presence of sodium acetate into 5-acenaphthylglycine,



plates, m. p. 210–212° (decomp.). The corresponding potassium salt becomes carbonised when treated with molten sodamide.

H. W.

The Preparation of cycloHexanol. ANDRÉ BROCHET (*Compt. rend.*, 1922, 175, 583–585; cf. A., 1914, i, 645).—Certain aspects of the reaction between hydrogen and phenol in presence of reduced nickel are dealt with. Values of the specific activity of nickel are given for a temperature range of 90°. The reaction should be carried out under pressure. No trace of a substance intermediate between phenol and cyclohexanol was found. The mechanism of the reaction does not depend on the method of hydrogenation, which may be effected in either the liquid or vapour phase; in the latter case, formation of cyclohexene, cyclohexane, and cyclohexanone may occur, but this is avoided by working at as low a temperature as possible. It is advisable to work with at least 5% of the catalyst, as repeated use causes the nickel to decrease considerably in activity, although such used nickel may be shown to be of almost full activity if used for hydrogenation of sodium cinnamate.

H. J. E.

The Action of Bromine on Nitrophenol-sulphonic and -sulphocarboxylic Acids. EUKLID SAKELLARIOS (*Ber.*, 1922, 55, [B], 2846–2853).—A series of instances has been examined

in which the sulphonic or carboxylic groups of substituted nitro-phenyl are displaced smoothly by bromine.

Potassium *o*-nitrophenol-4 : 6-disulphonate,
 $\text{NO}_2\cdot\text{C}_6\text{H}_2(\text{OH})(\text{SO}_3\text{K})_2\cdot\text{H}_2\text{O}$

(cf. Charnot and Pratt, A., 1909, i, 641), is obtained conveniently by dissolving phenol in fuming sulphuric acid (20%), nitrating the product with nitric acid (85%) and sulphuric acid (96%), diluting the mixture with water, and precipitating the salt directly by the addition of potassium chloride solution. It is reduced by zinc and hydrochloric acid or by concentrated sodium hydrogen sulphite solution to *potassium hydrogen o-aminophenol-4 : 6-disulphonate*, $\text{NH}_2\cdot\text{C}_6\text{H}_2(\text{OH})(\text{SO}_3\text{H})(\text{SO}_3\text{K})\cdot\text{H}_2\text{O}$. An aqueous solution of the potassium salt of the nitro-acid is converted by bromine dissolved in glacial acetic acid into *potassium 2-bromo-6-nitrophenol-4-sulphonate* and 4 : 6-dibromo-*o*-nitrophenol, m. p. 117.5°. The constitution of the potassium salt is established by the observations that it is transformed by further bromination into 4 : 6-dibromo-*o*-nitrophenol and by nitric acid into 2 : 4-dinitro-*o*-bromophenol, m. p. 118.5°.

According to Datta (A., 1921, i, 331), the bromination of *o*-nitrophenol-4-sulphonic acid yields 4 : 6-dibromo-*o*-nitrophenol; if, however, only one molecular proportion of bromine is used, 6-nitro-*o*-bromophenol-4-sulphonic acid is obtained. The latter acid is reduced by zinc dust and hydrochloric acid to 2-bromo-6-*amino*-phenol-4-sulphonic acid, colourless crystals.

Potassium 2 : 6-dinitrophenol-4-sulphonate is converted by bromination into 4-bromo-2 : 6-dinitrophenol, m. p. 78° (the m. p. 85.6° recorded in Richter's Lexicon is incorrect).

Potassium hydrogen 3-nitro-5-sulphosalicylate is converted by bromine in a similar manner into 4 : 6-dibromo-2-nitrophenol, m. p. 117.5°, and potassium 6-bromo-*o*-nitrophenol-4-sulphonate, the constitution of which is established by its further conversion into 4 : 6-dibromo-*o*-nitrophenol and 6-bromo-2 : 4-dinitrophenol. The nitrosulphosalicylic acid is therefore shown to be 3-nitro-5-sulpho-*o*-hydroxybenzoic acid.

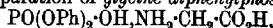
H. W.

Preparation of Di- and Poly-halogen Substitution Products of Monohydric Phenols. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.P. 349794; from *Chem. Zentr.*, 1922, iv, 45; cf. *Chemische Werke* Fehendorf, A., 1915, i, 674; Holleman, A., 1918, i, 216; 1921, i, 102).—Tri- and poly-halogen substitution products of aromatic hydrocarbons are heated at high temperatures under pressure with alkali hydroxides and methyl alcohol, or its homologues, with or without addition of other solvents. For example, 1 : 2 : 4 : 5-tetrachlorobenzene is heated with sodium hydroxide and methyl alcohol, with or without addition of pyridine, for about seven hours at 160° under pressure, or with potassium hydroxide and alcohol for about ten hours at 200°, or with potassium hydroxide and amyl alcohol for sixteen hours at 200° under pressure; whereby 2 : 4 : 5-trichlorophenol is obtained; it forms lustrous needles, m. p. 64—65°. 2 : 4 : 5-Tribromophenol is similarly prepared. 2 : 5-Dichlorophenol, from 1 : 2 : 4-trichlorobenzene, sodium

hydroxide, and methyl alcohol, has b. p. 211° , m. p. 58° . A mixture of polybromonaphthols may be prepared from mixed polybromonaphthalenes by similar means.

G. W. R.

Diphenylphosphoric Acid [Diphenyl Hydrogen Phosphate], a Reagent for the Amino-group. A. BERNTON (*Ber.*, 1922, 55, [B], 3361—3365).—Attempts to cause diphenylphosphoric chloride to react with copper glycine suspended in benzene were unsuccessful, but the addition of a little water to the mixture resulted in the separation of *glycine diphenylphosphate*,

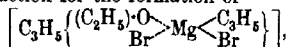


large, quadratic plates, m. p. $177-178^{\circ}$. The acid reacts with other amino-acids in aqueous solution, giving salts which crystallise in matted needles resembling cotton wool. The following are described: *alanine diphenylphosphate*, m. p. 193° ; *leucine diphenylphosphate*, m. p. 217° ; *glutamine diphenylphosphate*, m. p. 137° ; *glycylglycine diphenylphosphate*, m. p. 178° . *Methylamine diphenylphosphate* crystallises in thin, transparent plates, m. p. $78-79^{\circ}$; *ethylamine diphenylphosphate* forms small, colourless crystals, m. p. 126° , whereas *ammonium diphenylphosphate* has m. p. 130° . The acid, according to observations with acetamide and benzamide, does not appear to react with amides.

Diphenylphosphoric acid (+2 aq.) is most conveniently prepared by gradually adding diphenylphosphoric chloride to an aqueous solution of sodium hydroxide and subsequently warming the mixture on the water-bath, whereby the sodium salt (+ $5\text{H}_2\text{O}$), thick plates which melt at 70° in their water of crystallisation, is obtained; the free acid is precipitated by the addition of hydrochloric acid to an aqueous solution of the sodium salt. Silver diphenylphosphate has m. p. 213° .

H. W.

The Auxiliary Valency of the Hydroxyl Group. I. HANS REIHLEN (*Z. anorg. Chem.*, 1922, 123, 173—195).—The author reinvestigated the complex salts of pyrocatechol and its derivatives. He finds that the co-ordinated complex contains a water molecule, and that the reactions are only explained by assuming the co-ordination number to be four, and not six as suggested by Weiland (*A.*, 1914, i, 553). Thus the complex with iron as central metal is given the formula $[\text{Fe}(\text{H}_2\text{O})(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{O})_3]^{+++}$. Besides the two spheres (inner and outer, non-ionic and ionic), the author suggests a sphere between the two—non-ionic, but at the same time not under the full influence of the central atom. For example, in Grignard's reaction for the formation of



the allyl group is only loosely held but is non-ionic. Co-ordination is shown to depend, not only on the central atom, but also on the character of the negative groups. It is also shown that a hydroxyl group attached to the benzene nucleus loses its power of exerting auxiliary valency if its hydrogen atom receives ionic properties.

W. T.

The Auxiliary Valency of the Hydroxyl Group. The Complex Salts of Substituted Pyrocatechol. HANS REIHLEN and ADOLF SAPPER (*Z. anorg. Chem.*, 1922, **124**, 275—288).—Several complex salts with catechol and its derivatives are prepared; in these the author holds that the co-ordination number is four irrespective of the nature of the central atom. To explain the formation of the compound, the author assumes that the four groups are arranged at the corners of a tetrahedron around the central atom. The preparation and the properties of the following compounds are described, $[\text{Cu}_2(\text{C}_6\text{H}_4\text{O}_3)_4(\text{H}_2\text{O})_2]\text{Na}_4 \cdot 7\text{H}_2\text{O}$, $[\text{Zn}_2(\text{C}_6\text{H}_4\text{O}_3)_4(\text{H}_2\text{O})_2]\text{Na}_4 \cdot 18\text{H}_2\text{O}$, $[\text{Ni}(\text{C}_6\text{H}_3\text{O}_4)_2(\text{H}_2\text{O})_2]\text{Na}_4 \cdot 18\text{H}_2\text{O}$, $[\text{Ni}_2(\text{O}-\text{C}_6\text{H}_3\text{O}-\text{CO}_2\text{Et})_2(\text{H}_2\text{O})_2]\text{Na}_4 \cdot 25\text{H}_2\text{O}$, $[\text{Ni}_6(\text{C}_6\text{H}_4\text{O}_3)_{10}(\text{C}_6\text{H}_4\text{O}_2\text{OH})_2\text{H}_2\text{O}]\text{Na}_{11} \cdot 45\text{H}_2\text{O}$, $[\text{Ni}_5(\text{C}_6\text{H}_3\text{O}_4)_{10}(\text{C}_6\text{H}_4\text{O}_2\text{OH})(\text{OH})_4]\text{Na}_{12} \cdot 50\text{H}_2\text{O}$, $(\text{Cd}_6(\text{C}_6\text{H}_4\text{O}_3)_{12}(\text{C}_6\text{H}_4\text{O}_2\text{OH}))\text{Na}_{13} \cdot 54\text{H}_2\text{O}$. This cadmium compound is given a cyclic structure. W. T.

The Constitution of Resorcinol and some of its Derivatives. RENÉ FABRE (*Ann. Chim.*, 1922, **18**, 49—116).—The ketonic character of resorcinol, shown by Herzig and Zeisel from a study of ethylresorcinols (A., 1891, 75), was confirmed from the molecular refraction of the tetraethyl derivative. Ethylation of 4-chlororesorcinol results in the formation of a mixture of diethyl and triethyl derivatives, and in the latter (4-chloro-2:2-diethylresorcinol ethyl ether) only one of the ethyl groups is present as an ethoxy-group, the resorcinol behaving partly as a phenol and partly as a ketone. An isomeride of this substance is obtained by the action of sulphuryl chloride on triethylresorcinol. Attempts were made to obtain other derivatives in which resorcinol functions as a ketone (cf. Fuchs and Eisner, A., 1920, i, 545); these were unsuccessful. A study of nitrosoresorcinols showed that the nitroso-group enters in the 2-position if the 4-position is already substituted. Sodium resorcinoxide combines directly with carbon dioxide, giving, under a pressure of six atmospheres at 115—120°, 85% of the theoretical yield of sodium β -resorcyate (cf. Kostanecky, A., 1886, 242). Similar attempts at fixation of carbon dioxide with 4-chlororesorcinol showed that, as with the nitroso-derivatives, the fixation occurs in the 2-position if the 4-position is already substituted. The condensation of resorcinol with benzaldehyde was effected in acetic acid solution, yielding a crystalline product, benzyldene-resorcinol, which is soluble in alcohols of high boiling point. The substance gives an acetyl derivative of the formula $(\text{C}_{17}\text{H}_{14}\text{O}_4)_2$, and the inference is drawn that its formula is $\text{C}_{28}\text{H}_{20}\text{O}_4$; a study of analogous condensation products previously obtained (Liebermann, Lindenbaum, and Glave, A., 1904, i, 443; Pope and Howard, T., 1910, 97, 78) shows it to be similar to these, although a crystalline product had not been prepared. Structural formulae for this and the analogous substances obtained are suggested. Benzaldehyde does not react with tetraethylresorcinol, but with the triethyl derivative* condensation occurs; this appears to indicate that the aldehyde is linked in the para-position with

respect to one of the hydroxyl groups. Condensation products obtained from resorcinol with xanthydrool confirm the conclusion that the most easily replaceable hydrogen atom is that which occupies the 4-position, and thus is in the *para*-position with respect to hydroxyl; di-substitution takes place in the 2- and 4-positions. Although in some cases resorcinol behaves as a ketone, in the majority of instances it reacts as a phenol; the former type of reaction occurs in the case of condensations effected in presence of sodium methoxide, and the replaceable hydrogen is then that which is linked to the carbon atom situated between the two carbonyl groups.

The following substances do not appear to have been previously described. 4-Chloro-2:2-diethylresorcinol 3-ethyl ether, colourless needles, m. p. 25°. 4-Chloro-2-nitrosoresorcinol, yellow plates. 3-Chloro-2:4-dihydroxybenzoic acid, colourless needles, m. p. 209°. 3-Chloro-2:6-dihydroxybenzoic acid, colourless crystals, m. p. 215–216°. 2:4-Dihydroxy-3-xanthylbenzoic acid, colourless crystals, turning red and softening without melting at 200°. Acetylbenzylideneresorcinol, colourless, prismatic needles, m. p. 364–366°. 4-Benzylidene-1:2:3-triethylresorcinol, colourless needles, decompose on heating. Vanillideneresorcinol, pale rose crystals, from acetic acid, colourless needles, from benzyl alcohol, decompose on heating; acetyl derivative, m. p. 323°. Piperonylideneresorcinol, needles turning pink on exposure to light, resinify on heating; acetyl derivative, m. p. above 370°. 4-Xanthylresorcinol, colourless needles, m. p. 178–179°; diacetyl derivative, m. p. 242–243°. 2:4-Dixanthylresorcinol, colourless needles, m. p. 255–257°; diacetyl derivative, m. p. 262–263°. 4-Xanthyl-1:2-diethylresorcinol 3-ethyl ether, colourless crystals, m. p. 201–202°. 4-Nitroso-2-xanthylresorcinol, bright, dark red crystals, m. p. 212°. 2-Nitroso-4-xanthylresorcinol, golden-yellow, hexagonal crystals, m. p. 295–296°. 4-Chloro-2-xanthylresorcinol, colourless crystals, m. p. 215°. Xanthylquinol, pale greenish-yellow crystals, m. p. 215–216°. 2:3-Dixanthylquinol, colourless crystals, m. p. 231–232°. 3-Chloro-2-xanthylquinol, colourless crystals, m. p. 236–237°. Xanthylpyrocatechol, yellow crystals, m. p. 205–206°. 4:5-Dixanthylpyrocatechol, colourless crystals, m. p. 235–236°. 4-Chloro-3-xanthylpyrocatechol, colourless crystals, m. p. 224°. H. J. E.

Univalent Oxygen. I. STEFAN GOLDSCHMIDT (*Ber.*, 1922, 55, [B], 3194–3197).—If a solution of guaiacol in ether is treated during a few minutes with a large excess of lead peroxide at a low temperature, a very unstable green or bluish-green solution is obtained which exhibits the properties to be expected of a radicle with univalent oxygen. It is completely insensitive towards oxygen. It is immediately decolorised by quinol, phenylhydrazine, or a solution of triphenylmethyl in benzene. It does not react with nitric oxide. When cooled to -80° , the solution becomes much lighter in colour. The further investigation of the solutions and the isolation of any radicle which may be present is rendered exceedingly difficult by its great instability. Quan-

titative oxidation with phenylhydrazine shows that only a small fraction of the guaiacol has been oxidised in the direction indicated.

Similar observations are made during the oxidation of quinol monomethyl ether. The solutions are pure blue in colour and extraordinarily unstable. The change of colour with alteration in temperature is more pronounced than with guaiacol solutions. Under similar conditions, *o*-cresol gives a blood-red, α -naphthol a blue-red, and β -naphthol a pale green solution.

It appears reasonable to assume that the blue oxidation products of guaiacol and quinol methyl ether are formed by the removal of the hydrogen atom of the hydroxyl group, thus $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot$. This view, however, does not appear to be tenable, since the reduction product of oxidised guaiacol, after removal of guaiacol, can be re-oxidised to the blue substance. The constitution of the compound is still under investigation. H. W.

Univalent Oxygen. II. Phenanthroxylys. STEFAN GOLDSCHMIDT and WALTER SCHMIDT (*Ber.*, 1922, 55, [B], 3197-3215; cf. preceding abstract).—Phenanthraquinol monomethyl and monoethyl ethers are readily oxidised to colourless substances which are insoluble in alkali hydroxide and are distinguished from the parent material by containing one atom of hydrogen less in their molecule. They form greenish-yellow solutions which gradually darken when preserved. The occurrence of radicle dissociation is established by the failure of the solutions to obey Beer's law and by the dependence of molecular weight on dilution. The present cases of dissociation are distinguished by the long period which is necessary for the establishment of equilibrium which can be followed by periodical determination of molecular weight; constancy of the latter and of the colour of the solutions is attained simultaneously. The process is complete in about two and a half hours and in *N*/100 solution at the atmospheric temperature about 37%, of the methyl and 62% of the ethyl compound is dissociated into radicles. The constitution of the compounds is discussed in detail, and the authors draw the conclusion that the bimolecular products are to be regarded as 9-alkoxy(acyloxy)-10-phenanthryl peroxides, $\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{OR} \quad \text{RO}\cdot\text{C}\cdot\text{C}_6\text{H}_4$, and the unimolecular substances as $\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{O}\text{---}\text{O}\cdot\text{C}\cdot\text{C}_6\text{H}_4$, 9-alkoxy(acyloxy)-10-phenanthroxylys, $\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{OR}$, $\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{O}\text{---}$.

Phenanthraquinol monomethyl ether, $\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{OMe}$, colourless aggregates of small needles, m. p. 103° after darkening at 92°, is obtained in small yield by the action of methyl sulphate and potassium hydroxide on phenanthraquinol in the complete absence of air. The corresponding monoethyl ether (+EtOH) is prepared conveniently by the addition of finely divided phenanthraquinone to an ethereal solution of zinc ethyl. The preparation of the monoethyl compound by a corresponding alteration of this method

does not appear to be practicable; the course of the change is not very obvious, but the ultimate product is *phenanthraquinol dimethyl ether*, needles, m. p. 87°. Phenanthraquinol monoacetate, colourless needles, m. p. 170° (decomp.), is obtained conveniently by short treatment of the quinol with hot acetic anhydride.

Oxidation of the monomethyl ether dissolved in aqueous potassium hydroxide solution by means of potassium ferricyanide gives *9-methoxy-10-phenanthryl peroxide*, almost colourless crystals, m. p. 165° (decomp.), to a pale brown mass. The substance combines with triphenylmethyl in benzene solution, but the additive compound shows little tendency to crystallise, and is identified by hydrolysing it with dilute sodium hydroxide solution to triphenylcarbinol and the original ether. It is reduced by the action of zinc dust and glacial acetic acid on its solution in ether to phenanthraquinol monomethyl ether, m. p. 102–103°, and converted slowly by oxygen in the presence of benzene to phenanthraquinone. It does not react with nitric oxide.

Phenanthraquinol monoethyl ether is converted by potassium ferricyanide in the presence of aqueous potassium hydroxide solution or by lead peroxide in the presence of ether and anhydrous potassium carbonate into *9-ethoxy-10-phenanthryl peroxide*, almost colourless aggregates of needles ($+2C_6H_6$), m. p. 138° (decomp.). It unites with triphenylmethyl, and the additive compound is hydrolysed (as in the case of the methyl compound) to triphenylcarbinol and phenanthraquinol monomethyl ether. It is reduced by zinc dust and glacial acetic acid, phenylhydrazine, quinol, or hydriodic acid to phenanthraquinol monoethyl ether; with the reagent last-mentioned, the reduction is practically quantitative. The radicle, when dissolved in benzene, is slowly converted by oxygen into phenanthraquinone and ultimately into diphenic acid. It does not react with nitric oxide. It immediately decolorises a solution of bromine in chloroform, by which it is converted into phenanthraquinone. It does not react smoothly with potassium in the presence of benzene, since the metal is only superficially attacked. With potassium phenyl diphenyl ketone the green solution is rapidly decolorised with formation of the *potassium salt* which is decomposed with production of the pure ethyl ether.

Phenanthraquinyl monoacetate, suspended in anhydrous ether, is oxidised by lead peroxide to a compound, $C_{32}H_{22}O_6$, colourless, rhombic crystals, m. p. 208–209° (decomp.). Its solutions in all solvents are colourless, even when warmed. In boiling ethyl benzoate a yellow colour is observed which is due to decomposition. The substance does not react with phenylhydrazine in the presence of chloroform.
H. W.

Chlorination of Benzoyl Chloride. I. EDWARD HOPE and GEORGE CLIFFORD RILEY (T., 1922, 121, 2510–2527).

Dealkylation of Mixed Secondary Bases by Phosphorus Chloride. JULIUS VON BRAUN and JOSEF WEISMANTEL (Ber., 1922, 55, [B], 3165–3170).—The relative affinity of the alkyl groups for nitrogen has been determined for the reaction:

$\text{NHR}^1\text{R}^2 \rightarrow \text{NR}^1\text{R}^2\text{-COPh} \xrightarrow{+\text{PCl}_5} \text{NR}^1\text{R}^2\text{-CCl}_2\text{Ph} \rightarrow \text{R}^1\text{Cl} + \text{NR}^2\text{CClPh} \rightarrow \text{R}^2\text{Cl} + \text{NH}_2\text{R}^1$. The series may be arranged in the sequence: benzyl, methyl, ethyl, propyl, *n*-butyl; so, for example, benzylmethylamine yields methylamine. It is remarkable that the order is precisely the same as in the cyanogen bromide reaction which is effected at 0° , whereas the present change is carried out at about 140° .

Benzomethylbenzylamide, m. p. 44° (cf. Lander, P., 1903, 19, 45), is converted by phosphorus pentachloride at 110° and subsequent treatment with water into benzyl chloride and benzo-methylamide, b. p. $164\text{--}165^\circ/15\text{ mm.}$, m. p. 80° . Benzomethyl-ethylamide, b. p. $163\text{--}165^\circ/27\text{ mm.}$ (cf. Titherley, T., 1901, 79, 407) at 140° yields methyl chloride and benzoethylamide, m. p. 68° . Benzoethylpropylamide, b. p. $158\text{--}160^\circ/12\text{ mm.}$, gives ethyl chloride and benzopropylamide.

When propylamine is treated with benzenesulphonyl chloride, the resulting amide is converted by *n*-butyl bromide into *benzenesulphonpropyl-n-butylamide*, $\text{SO}_2\text{Ph-NPr-C}_4\text{H}_9$, a colourless liquid, b. p. $202\text{--}204^\circ/12\text{ mm.}$; this is transformed in the usual manner into *propyl-n-butylamine*, b. p. $134\text{--}135^\circ$ (*hydrochloride*, m. p. 255°). *Benzopropyl-n-butylamide* is converted by phosphorus pentachloride at 150° into propyl chloride and benzo-*n*-butylamide.

H. W.

Preparation of a Basic Aluminium Salicylate. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (D.R.-P. 354698; from *Chem. Zentr.*, 1922, iv, 377).—A basic aluminium salicylate of the formula $\text{OH-C}_6\text{H}_4\text{-CO}_2\text{-Al(OH)}_2$ is obtained by mixing aluminium hydroxide with salicylic acid, if necessary, with the application of heat. The product is a colourless or slightly red powder. It is distinguished from the normal salt by its stability in the presence of water and dilute acids and on warming.

G. W. R.

Derivatives of Dulcin. PAUL HERMANN (*Annalen*, 1922, 429, 163—174).—3-Carbamido-6-methoxybenzoic acid has m. p. $187\text{--}193^\circ$, and is soluble in 125 parts of hot [$? \text{boiling}$] water or 400 parts of water at 15° ; the solution has a sour taste. The *ethyl* ester melts at $191\text{--}192^\circ$. 3-Thiocarbamido-6-methoxybenzoic acid, m. p. $205\text{--}206^\circ$, is insoluble in cold water, and has a faintly sour taste. 3-Carbamido-6-ethoxybenzoic acid forms colourless, small needles, m. p. $195\text{--}196^\circ$, soluble in 40 parts of hot water and in 660 parts of water at 15° , and has a faintly sour taste. Its *ethyl* ester, m. p. $179.5\text{--}180.5^\circ$, has a bitter taste. 3-Thiocarbamido-6-ethoxybenzoic acid forms needles, m. p. $182\text{--}183^\circ$, and is soluble in 90 parts of boiling water; it has a feebly sour taste. 4-Carbamido-1-ethoxynaphthalene forms small needles which sinter at $205\text{--}207^\circ$, m. p. $264\text{--}265^\circ$ (decomp.); it has a bitter taste. 4-Thiocarbamido-1-ethoxynaphthalene has m. p. $210.5\text{--}211.5^\circ$, and has a very bitter taste in alcoholic solution. These substances are all formed by the action of potassium cyanate or ammonium thiocyanate on the appropriate amine. 3:3-Carbamidebis-6-methoxy-

benzoic acid is obtained when methoxyaminobenzoic acid is heated with carbamide. It has m. p. 243° (decomp.). C. K. I.

Anhydrides of *N*-Carboxylic Acids. FRIEDRICH FUCHS (*Ber.*, 1922, 55, [B], 2943).—In connexion with the recent observations of Curtius and Sieber (this vol., i, 721), it is pointed out that phenyl-

glycine anhydride, $\text{NPh} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$, can be obtained in good yield

by the action of carbonyl chloride on a cold, alkaline solution of phenylglycine. With aniline and alcohols, it gives the anilide and esters of phenylglycine. The *N*-carboxylic anhydride derived from *p*-tolylglycine is more stable and better adapted to further investigation than the lower homologue. H. W.

The Resin Acids of the *Coniferae*. V. The Nitrosochloride, Nitrosite, and Nitrosate of Pinabietic Acid and Abietic Acid [Levy]. Constitution of Abietic Acid and Abietine. OSSIAN ASCHAN [with NILS FONTELL and P. E. SIMOLA (*Ber.*, 1922, 55, [B], 2944—2959; cf. this vol., i, 221, and previous abstracts).—Pinabietic acid has been isolated from pine oil and characterised as a homogeneous substance by Aschan and his co-workers (*A.*, 1921, i, 669); its constitution has been established except for certain details by Virtanen (*A.*, 1921, i, 669). The acid is very similar to the abietic acid of Levy (*A.*, 1907, i, 947; 1910, i, 11) and Johansson (*A.*, 1920, i, 232). The two acids give nitrosochlorides, nitrosites, and nitrosates which are most probably identical, and also the same colour changes in Liebermann's cholesterol reaction. It is therefore most probable that the acids are structurally identical. Certain differences are, however, apparent in their optical properties (as will be shown later) so that the possibility of stereoisomerism is not excluded. The strongest argument against the structural identity of the acids lay in the observation of Levy (*loc. cit.*) that abietic acid is converted by cold potassium permanganate into a well-defined tetrahydroxy-acid, $\text{C}_{19}\text{H}_{29}(\text{OH})_4 \cdot \text{CO}_2\text{H}$, of high melting point, whereas the similarly prepared product from pinabietic acid is a crystalline, apparently saturated, monocarboxylic acid of low melting point (the details of which will be given later). Repetition of Levy's experiments has failed to yield the tetrahydroxy-acid, which is presumed to have owed its origin to associated silvic acid. Levy's abietene and Virtanen's pinabietene must also be regarded as structurally identical 7:13-dimethyl-2-isopropyl-5:6:7:8:9:10:13:14-octahydrophenanthrene. For the parent hydrocarbon the name *phen-octalin* is proposed, on account of its similarity to tetralin [tetrahydronaphthalene].

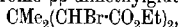
[With NILS FONTELL and P. E. SIMOLA].—Pinabietic acid nitrosochloride, $\text{HO} \cdot \text{N} \cdot \text{C}_{19}\text{H}_{29} \text{Cl} \cdot \text{CO}_2\text{H}$, is prepared by passing hydrogen chloride into a solution of pinabietic acid and ethyl or amyl nitrite in glacial acetic acid. It crystallises in lustrous, very voluminous needles, m. p. 144 — 145° . (The sodium salt is described.) It is converted by a boiling solution of sodium in ethyl alcohol (90%) into *oximinopinabietic acid*, $\text{HO} \cdot \text{N} \cdot \text{C}_{19}\text{H}_{27} \cdot \text{CO}_2\text{H}$, a brownish-yellow

powder, decomp. about 130° after incipient softening at 120° . The nitrosite of pinabietic acid, $\text{OH}\cdot\text{N}\begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix}\text{C}_{19}\text{H}_{28}\cdot\text{CO}_2\text{H}$, is obtained by the gradual addition of concentrated hydrochloric acid to a solution of pinabietic acid in benzene which is floating on an aqueous solution of sodium nitrite; it is a colourless, voluminous, crystalline powder which softens at about $75\text{--}76^{\circ}$ and is generally completely molten at about $120\text{--}130^{\circ}$. Pinabietic acid nitrosate, a voluminous, yellow powder, decomp. $72\text{--}73^{\circ}$, is prepared by the gradual addition of concentrated nitric acid ($d\ 1.4$) to a well-cooled solution of pinabietic acid and amyl nitrite in glacial acetic acid.

The following compounds are prepared from abietic acid obtained from American colophony by Levy's method; the specimen used was not quite homogeneous, having m. p. $167\text{--}170^{\circ}$ instead of $181\text{--}183^{\circ}$. Nitrosochloride, m. p. 140° ; nitrosite, which softens and evolves gas at 76° ; nitrosate, a yellow powder which softens at 72° . The melting or decomposing points of these substances are unchanged by admixture with the respective corresponding compounds derived from pinabietic acid.

Further work (as yet unpublished) makes it probable that pinabietic and abietic acids are completely identical. H. W.

Attempted Synthesis of Norpinic Acid. KANAI LAL GANGULY (*J. Indian Inst. Sci.*, 1922, 5, 23—28).—Verification of the structure of norpinic acid by synthesis is of importance on account of its close relationship to pinene and the products derived therefrom. An attempt was made to synthesise norpinic acid by condensing ethyl α -dibromo- β -dimethylglutarate,

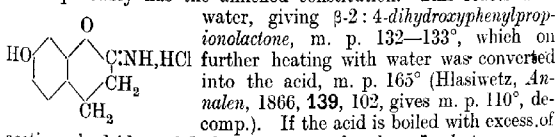


with methylene bromide or iodide by means of sodium in benzene. A very small amount of crystalline product, m. p. 172° , which might have been *cis*-norpinic acid, was obtained, but the experiment cannot be regarded as successful. E. H. R.

Condensation of certain Nitriles and Various Polyhydroxyphenols to form Phenolic Acids. WILSON D. LANGLEY and

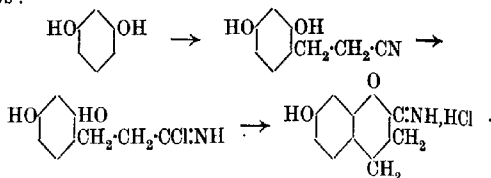
ROGER ADAMS (*J. Amer. Chem. Soc.*, 1922, 44, 2320—2330).—

Unlike chloroacetonitrile (cf. Sonn, A., 1918, i, 31), β -chloropropionitrile does not condense normally with resorcinol. In dry ether in the presence of anhydrous zinc chloride and hydrogen chloride, β -chloropropionitrile and resorcinol give first a white solid, which probably has the annexed constitution. This reacts with



water, giving β -2:4-dihydroxyphenylpropionolactone, m. p. $132\text{--}133^{\circ}$, which on further heating with water was converted into the acid, m. p. 163° (Hlasiwetz, *Annalen*, 1866, 139, 102, gives m. p. 110° , decomp.). If the acid is boiled with excess of acetic anhydride, β -2-hydroxy-4-acetoxyphenylpropionolactone, m. p. 112° , is obtained. Acrylonitrile may be used instead of β -chloropropionitrile in the above condensation. β -2:4-Dimethoxyphenylpropionic acid, m. p. $102.5\text{--}103.5^{\circ}$, was obtained by the direct methyl-

ation of the dihydroxy-acid, and by the action of butyl nitrite the dihydroxy-acid gave β -5-nitroso-2:4-dihydroxyphenylpropionolactone, m. p. 147.5—148°. Resorcinol monomethyl ether and β -chloropropionitrile gave β -2-hydroxy-4-methoxyphenylpropionic acid, m. p. 138—139.5°, together with the lactone, and the nitrile, m. p. 126.5—127.5°, as intermediate products. The suggested mechanism of the condensation of resorcinol and of β -chloropropionitrile is as follows:



Under similar conditions, orcinol gives with β -chloropropionitrile or acrylonitrile β -3:5-dihydroxy-o-tolylpropionolactone, m. p. 140—141.5°. Similarly, phloroglucinol gives β -2:4:6-trihydroxyphenylpropionolactone, a viscous oil.

Resorcinol and γ -chlorobutyronitrile react in dry ether in the presence of zinc chloride and hydrogen chloride to give γ -2:4-dihydroxyphenylbutyric acid, m. p. 118.5—119°, and in this case the lactone could not be obtained.

W. G.

Preparation of Sodium and Potassium Phthalimide.

DALZIEL LLEWELLYN HAMMICK and GEORGE HAZLEWOOD LOCKET (T., 1922, 121, 2362—2363).

Derivatives of Amino-aldehydes. ERICH RADDE (Ber., 1922, 55, [B], 3174—3179).—A number of attempts are recorded to prepare amino-aldehydes of the aliphatic series by the reduction of amino-acids in which the basic group is protected by the presence of the phthalyl radicle; complete success, however, has not been attained.

Phthalimino- α -hydroxy-propionic and -butyric acids lose carbon dioxide when heated with sulphuric acid, but an aldehydo-compound cannot be isolated from the resinous substances which are produced (Gabriel, A., 1907, i, 625; Gabriel and Colman, A., 1908, i, 274); the use of phosphoric acid, thionyl chloride, or hydrochloric acid in place of sulphuric acid does not lead to improved results.

Phthalylglycylanilide, $\text{C}_8\text{H}_4\text{O}_2\text{N} \cdot \text{CH}_2\text{CO} \cdot \text{NHPh}$, aggregates of needles, m. p. 227°, is converted by phosphorus pentachloride in the presence of benzene into the corresponding chloro-compound, $\text{C}_8\text{H}_4\text{O}_2\text{N} \cdot \text{CH}_2 \cdot \text{CCl} \cdot \text{NPh}$, needles, m. p. about 90°; reduction of the imino-chloride with stannous chloride according to the method of Sonn and Müller (A., 1920, i, 58) does not give an aldehydo-compound.

The action of hydrocyanic acid and pyridine on a solution of phthalylglycyl chloride in anhydrous ether gives the compound,

$C_8H_4O_2 \cdot N \cdot CH(CO \cdot CN) \cdot CO \cdot CH_2 \cdot N \cdot C_8H_4O_2$, needles, m. p. 203.5—205.5° (decomp.), instead of the expected phthalylglycyl cyanide.

Attempts to convert phthalylglycylanilide chloride into the corresponding amidine or to reduce phthalylglycyl esters to aldehydes by sodium amalgam in acid solution were unsuccessful.

Phthalylglycylamide, $C_8H_4O_2 \cdot N \cdot CH_2 \cdot CO \cdot NH_2$, needles, m. p. 257°, is converted by thionyl chloride or, preferably, by distillation with phosphoric oxide into *phthalylglycylonitrile*, $C_8H_4O_2 \cdot N \cdot CH_2 \cdot CN$, four-sided plates, m. p. 124—126°, which can also be prepared from chloroacetonitrile and potassium phthalimide at 120°. The nitrile could not be converted into the corresponding imino-ether, from which it might have been reduced to the aldehyde according to the method of Heale (A., 1905, i, 490).

A solution of phthalylglycyl chloride in toluene is reduced by hydrogen in the presence of palladised barium sulphate and "sulphured" quinoline in accordance with the procedure of Rosenmund and Zetsche to *phthalimidoacetaldehyde*, $C_8H_4O_2 \cdot N \cdot CH_2 \cdot CHO$, needles, m. p. 113—114.5° (*phenylhydrazone*, yellow needles, m. p. 163—165°; *oxime*, clusters of needles, m. p. 166—168°; *semicarbazone*, needles, m. p. 233—244°). The hydrolysis of phthalimidoacetaldehyde is invariably accompanied by the liberation of ammonia. α -Phthalimidopropionyl chloride is similarly reduced to α -*phthalimidopropaldehyde*, $C_8H_4O_2 \cdot N \cdot CHMe \cdot CHO$, needles, m. p. 108.5—111° (*semicarbazone*, needles, m. p. 225.5—226.5°), which also yields ammonia when hydrolysed by hydrochloric acid. Similar unsuccessful results are obtained with compounds containing the phthalimido-residue in the β -, γ -, or δ -position. The following observations are incidentally recorded. Ethyl β -phthalimidoethylmalonate, $C_8H_4O_2 \cdot N \cdot CH_2 \cdot CH_2 \cdot CH(CO_2Et)_2$, is transformed by hydrobromic acid (*d* 1.49) into β -*phthalimidoethylmalonic acid*, needles, m. p. 168° (decomp.) (the ammonium salt and the methyl ester, m. p. 64—65°, are described); the decomposition of the acid by heat gives a convenient method for the preparation of γ -phthalimido-*n*-butyric acid. δ -Phthalimido-*n*-valeric acid is similarly prepared from γ -phthalimido-*n*-propylmalonic esters; γ -*phthalimido-*n*-propylmalonic acid*, $C_8H_4O_2 \cdot N \cdot (CH_2)_3 \cdot CH(CO_2H)_2$, has m. p. 165° (decomp.).

Phthalylglycylonitrile is converted by a boiling solution of sodium methoxide and subsequent treatment with ammonium chloride into the ammonium salt, $NH_4 \cdot CO_2 \cdot C_8H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CN$, prisms, m. p. about 240° (decomp.) [the corresponding silver salt, needles, and free acid, needles, m. p. 138—139° (decomp.) are described]; sodium ethoxide behaves similarly, but yields a less pure product. The action of the alkali consists essentially in the opening of the ring and does not lead to the production of an isoquinoline derivative, as would be expected from the observations of Gabriel and Colman (*loc. cit.*) on the behaviour of phthalylglycyl esters under similar conditions. *Phthalyl- α -alanylamide*, $C_8H_4O_2 \cdot N \cdot CHMe \cdot CO \cdot NH_2$, m. p. 211—212° (prepared from the corresponding chloride and gaseous ammonia in the presence of benzene), is converted by distillation with phosphoric oxide into

the nitrile, $C_8H_4O_2 \cdot N \cdot CHMe \cdot CN$, four-sided plates, m. p. 139–140°. The latter is transformed by sodium ethoxide into the sparingly soluble ammonium salt, $NH_4 \cdot CO_2 \cdot C_8H_4 \cdot CO \cdot NH \cdot CHMe \cdot CN$, which is reconverted into the original material when treated with hydrochloric acid.

H. W.

Dyes Derived from "Saccharin." The Sulphamphthaleins. SIKHIBHUSHAN DUTT (T., 1922, 121, 2389–2394).

The Relationship between the Dimeric Ketens and cyclo-Butane-1:3-dione and its Derivatives. W. DIECKMANN and ADOLF WITTMANN (*Ber.*, 1922, 55, [B], 3331–3347).—The dimeric alkylketencarboxylic esters and a series of other dimeric ketens have been regarded by Schroeter (A., 1917, i, 145; 1920, i, 852) as "polymolecules" in which the monomeric components are not united by main or subsidiary atomic valencies, but by molecular valencies. This conception has been criticised adversely by Staudinger (A., 1920, i, 517). An extended examination of the question leads the author to the conclusion that Schroeter's views are untenable.

Schroeter's conclusions are based on the established difference in properties between the products obtained by the action of chloroformic esters on dialkylcyclobutanedionemonocarboxylic esters and those derived by the polymerisation of monomeric alkylketencarboxylic esters. He regards the conception of the former as

O-derivatives, $CMe \langle \begin{smallmatrix} C(O \cdot CO_2R) \\ CO \end{smallmatrix} \rangle CMe \cdot CO_2R$, as erroneous. A con-

sideration of analogous cases leads the author to consider it as probable, but conclusive evidence in favour of this view is afforded by the observation that methyl 2-ethylcarbonato-1:3-dimethylcyclo-

butene-4-one-3-carboxylate, $CMe \langle \begin{smallmatrix} C(O \cdot CO_2Et) \\ CO \end{smallmatrix} \rangle CMe \cdot CO_2Me$, colour-

less crystals, m. p. 66–68°, b. p. 173–175°/11 mm. (obtained from ethyl chloroformate and methyl dimethylcyclobutanedionecarboxylate) differs from ethyl 2-methylcarbonato-1:3-dimethylcyclo-

butene-4-one-3-carboxylate, $CMe \langle \begin{smallmatrix} C(O \cdot CO_2Me) \\ CO \end{smallmatrix} \rangle CMe \cdot CO_2Et$, a colour-

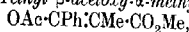
less liquid, b. p. 173–175°/11 mm., which does not solidify (prepared from methyl chloroformate and ethyl dimethylcyclobutanedionecarboxylate), whereas if, according to Schroeter, the new group had become attached to a carbon atom, the compounds must be identical, thus $CO_2Me \cdot CMe \langle \begin{smallmatrix} CO \\ CO \end{smallmatrix} \rangle CMe \cdot CO_2Et$. The esters

when treated with sodium alkoxide re-form methyl and ethyl 2:4-dimethylcyclobutanedionecarboxylates, respectively. The difference of these esters from the dimeric alkylketencarboxylic esters cannot be regarded as an argument against the conception of the latter as unitary dialkylcyclobutanedionedicarboxylic esters.

A further argument in favour of the "polymolecular" structure of the dimeric alkylketencarboxylic esters has been based by Schroeter (*loc. cit.*) on their catalytic decomposition in alcoholic solution by a trace of sodium alkoxide whereby two molecules of

alkylmalonic esters are produced. The same property is, however, observed in the acyclic analogues of the dialkylcyclobutanedione-carboxylic esters, for example, acetylalkylmalonic ester and α -di-aryl- α -methylacetic esters, which are beyond doubt unitary compounds containing the group $\begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{CR} \cdot \text{CO}_2\text{R}$. All these com-

pounds resemble the dimeric alkylketencarboxylic esters in that they are stable towards boiling alcohol but are catalytically decomposed with evolution of heat when a trace of sodium alkoxide is added to the alcoholic solution. Contrary to Schroeter's assumption, fusion invariably occurs in such a manner that an acyl and not an alkylcarbonato-group is eliminated. The following examples are quoted: *Methyl α -benzoyl- α -methylacetoacetate*, $\text{CH}_3\text{CO} \cdot \text{CMeBz} \cdot \text{CO}_2\text{Me}$, colourless crystals, m. p. $79-80^\circ$, b. p. $173-174^\circ/10$ mm., prepared by the action of a solution of benzoyl chloride in ether on an ethereal suspension of methyl methylsodioacetoacetate, is transformed by methyl alcohol and sodium methoxide into methyl acetate and methyl α -benzoylpropionate, b. p. $141-142^\circ/10$ mm. *Methyl β -acetoxy- α -methylcinnamate*,

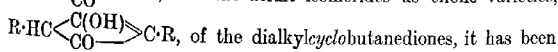


b. p. $161^\circ/10$ mm., prepared by the action of acetyl chloride on methyl α -methylsodiobenzoylacetate in the presence of ether, is converted in a similar manner into methyl α -methylbenzoylacetate, b. p. $143-144^\circ/10$ mm. Methyl acetylmethylacetoacetate ($\text{CH}_3\text{CO} \cdot \text{CMe} \cdot \text{CO}_2\text{Me}$ or $\text{CH}_3\text{C}(\text{OAc}) \cdot \text{CMe} \cdot \text{CO}_2\text{Me}$, b. p. $108^\circ/13$ mm., gives methyl methylacetoacetate. Ethyl acetyl ethylmalonate, $\text{CH}_3\text{CO} \cdot \text{CEt}(\text{CO}_2\text{Et})_2$, yields ethyl ethylmalonate, whilst methyl acetylmethylmalonate is converted into methyl methylmalonate.

Methyl dimethylacetoacetate is converted by contact with a solution of an approximately equivalent quantity of sodium ethoxide in ethyl alcohol during about an hour at the atmospheric temperature into ethyl dimethylacetoacetate; after a few days it is transformed into ethyl isobutyrate. Ethyl diethylacetoacetate is unchanged by the short action of sodium methoxide in methyl alcohol, but after five days it is transformed into methyl diethylacetoacetate; fission does not appear to occur. The esters of benzoic, succinic, and phthalic acid suffer transformation in the course of a few hours.

The behaviour of the dimeric alkylketencarboxylic esters towards aniline has not yet been fully explained, and appears to require further examination.

Against the conception of the dimeric ketens as ketonic forms, $\text{R} \cdot \text{HC} \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{CHR}$, and the acidic isomerides as enolic varieties,

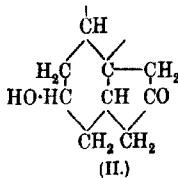
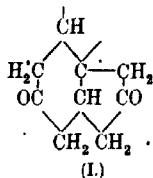


urged by Schroeter that the latter are indifferent towards the alkali metals in inactive solvents. This argument does not appear to be valid, since, on the one hand, compounds poor in or free from the enolic forms such as alkyl- β -ketocarboxylic esters and malonic or alkylmalonic esters react relatively readily with sodium,

whereas undoubted enols, for example, phenylhydroresorcinol and succinylsuccinic esters, can exhibit the same inactivity towards the metal as is observed by Schroeter in the case of the acidic forms of the dialkylcyclobutanediones. As further evidence in favour of the enolic form, it is shown that the acid dimethylcyclobutanedionecarboxylic ester and the acid diphenylcyclobutanedione behave as mono-enols when titrated with bromine in alcoholic solution, and are stable as such when dissolved in alcohol. The behaviour of dimeric phenylketen is in harmony with the conception that it is the ketonic form of diphenylcyclobutanedione. Its slow conversion into the acid form in indifferent solvents in the absence of catalysts and rapid transformation in the presence of alkali are precisely similar to the phenomena frequently observed in cases of keto-enolic desmotropy. Its conversion by ammonia into diphenylacetoacetamide and the acidic diphenylcyclobutanedione is readily explained by the assumption of simultaneous enolisation and ring fission.

H. W.

The Constitution of the Bile Acids. IV. Reductodehydrocholic Acid. W. BORSCHKE and F. HALLWASS (*Ber.*, 1922, 55, [B], 3318—3323).—Reductodehydrocholic acid, $C_{24}H_{42}O_5$, a hydroxy-diketonic acid of the cholic acid series, has been obtained previously by the action of sodium amalgam on dehydrocholic acid or by electrolytic reduction of the latter at a lead cathode. It is now prepared by the catalytic hydrogenation of dehydrocholic acid dissolved in glacial acetic acid in the presence of palladium black; it crystallises in colourless, slender needles which soften at 112° owing to loss of water of crystallisation (the *monohydrate* is described) and have m. p. 186—187°. Reductodehydrocholic acid dioxime (cf. Schenk, A., 1910, i, 10) has m. p. 255° (decomp.). Ethyl reductodehydrocholate is converted by aluminium amalgam in the presence of ether and benzene into *ethyl reductodehydrocholate*, coarse, colourless prisms, m. p. 153—154° (*dioxime*, colourless leaflets, m. p. 239—240°). *Methyl reductodehydrocholate*, prepared by esterification of the acid, crystallises in coarse needles, m. p. 155—156°, whereas its *dioxime* forms colourless leaflets, m. p. 258° (slight decomp.). Ethyl reductodehydrocholate is converted by distillation under diminished pressure into *ethyl diketocholenate*, long, colourless needles, m. p. 143° (*dioxime*, unctuous leaflets, m. p. 228°; *diketocholenic acid*, colourless prisms, m. p. 174°), which



is smoothly hydrogenated in alcoholic solution in the presence of spongy palladium to ethyl β -diketochol-
anate, m. p. 152—153°, identical with the compound described by Borsche and Wieckhorst (A., 1921, i, 729). Dehydrocholic acid

(I), and reductodehydrocholic acid (II) are therefore related to one another as indicated by the annexed formulæ.

Reduction of the ketonic group in ethyl α - or β -diketocholanates cannot be effected by means of aluminium amalgam. This is more surprising in the case of the α -compound, since α -diketocholanic acid is readily reduced by sodium amalgam and water to a hydroxyketocholanic acid, $C_{24}H_{38}O_3$ (monohydrate and anhydrous), colourless needles, m. p. about 160° after much softening at about 107° , which is probably identical with the acid described by Wieland and Boersch (A., 1919, i, 572). The corresponding ethyl ester has m. p. $131-132^\circ$ (Wieland and Boersch, m. p. 133°).

Bilanic acid is not affected by treatment with sodium amalgam in aqueous alkaline solution; its trimethyl ester is only slowly and incompletely attacked by aluminium amalgam in the presence of moist ether.

H. W.

The Constitution of the Bile Acids. V. Transformations from the Cholic to the Lithocholic Acid Series. W. BORSCHÉ and F. HALLWASS (Ber., 1922, 55, [B], 3324-3331).—Lithocholic acid, $C_{24}H_{40}O_3$, has been proved by Wieland and Weyland (A., 1921, i, 178) to be a normal constituent of bile. It is a monohydroxycholenic acid which is oxidised by nitric acid to lithobilanic acid, corresponding with bilanic acid; it is therefore probable that the hydroxy-group is attached to the same carbon atom as in cholic acid. This supposition has now been confirmed by the transformation of cholic acid through reductodehydrocholic acid into lithocholic acid.

Reductodehydrocholic acid (Borsche and Hallwass, preceding abstract) is reduced by amalgamated zinc and hydrochloric acid to resinous products and cholanolic acid. The formation of the latter substance is somewhat surprising, since it appears impossible to reduce cholic directly to cholanolic acid by this method. More satisfactory results are obtained by Wolff's method, according to which *reductodehydrocholic acid disemicarbazone*, $C_{26}H_{42}O_3N_6$, a white, chalky powder which becomes brown but does not melt at about 300° , is heated with an alcoholic solution of sodium ethoxide at 180° (the exact maintenance of the temperature is important), whereby it becomes transformed into lithocholic acid, colourless leaflets, m. p. $185-186^\circ$, $[\alpha]_D^{20} +32.72^\circ$, in absolute alcohol. Direct comparison shows that the acid is identical with the product obtained by Wieland and Weyland, the only point of difference being that its optical activity is greater. The acid is converted by an ethereal solution of diazomethane into *methyl lithocholate*, long needles, m. p. 130° , and by oxidation with nitric acid into lithobilanic acid (cf. Wieland and Weyland, *loc. cit.*). It has also been transformed into dehydrolithocholic acid, $C_{24}H_{38}O_3$, leaflets, m. p. 141° (cf. Wieland and Weyland, *loc. cit.*), the *methyl ester* of which, colourless leaflets, m. p. 117° , and *methyl ester oxime*, long needles, m. p. 148° , are described.

Dehydrocholic acid trisemicarbazone, an amorphous powder which becomes brown at about 290° and decomposes completely at a slightly higher temperature, is converted by a solution of sodium ethoxide in alcohol at 200° into cholanolic acid. *Bilanic acid di-*

semicarbazone, broad, colourless needles which become brown above 280° , is transformed in a similar manner into lithobilianic acid, m. p. 279° (cf. Wieland and Weyland, *loc. cit.*); the latter acid is obtained rather more readily under precisely similar conditions from *deoxybilianic acid semicarbazone*, $C_{25}H_{49}O_7N_3$, a colourless, amorphous solid, decomp. $215-220^{\circ}$. *Methyl lithobiliate*, $C_{27}H_{44}O_8$, crystallises in long, colourless needles, m. p. 112° .

isolithobilianic acid, small, colourless needles, m. p. 261° (decomp.), is obtained by the reduction of *isobilianic acid* dissolved in glacial acetic acid with amalgamated zinc and fuming hydrochloric acid (*methyl isolithobiliate* crystallises in colourless, lustrous leaflets, m. p. $103-104^{\circ}$). For some unexplained reason, and in spite of the apparent identity of the conditions, the action does not always take place smoothly, and the product frequently contains much *isodeoxybilianic acid* and other intermediate compounds. A more certain method for the preparation of *isolithobilianic acid* consists in the treatment of *isobilianic acid disemicarbazone* (an amorphous substance which darkens at about 280° and decomposes gradually at a higher temperature) with sodium ethoxide.

H. W.

Preparation of an Unsaturated Bile Acid. J. D. RIEDEL, AKT.-GES. (D.R.-P. 352129; from *Chem. Zentr.*, 1922, iv, 161).—Bromine is added to the acid prepared by an earlier patent (A., 1921, i, 540) and the product treated with alkalis. The *dibromide* obtained by the action of bromine on the acetic acid compound of *apocholic acid*, $C_{24}H_{38}O_4 \cdot C_2H_3O_2$, is a light yellow, heavy oil. By saponification with dilute alkali and addition of excess of dilute hydrochloric acid, an *unsaturated bile acid*, needles, m. p. $245-247^{\circ}$, is obtained. It is strongly antiseptic and has therapeutic uses.

G. W. R.

Derivatives of Diphenylthiolbenzene. SAMUEL SMILES and HUGH GRAHAM (T., 1922, 121, 2506—2510).

The Solubility and Volatility of the Nitrobenzaldehydes. NEVIL VINCENT SIDGWICK and WILFRED MARSDEN DASH (T., 1922, 121, 2586—2592).

α -Aldehydes of Tetrahydronaphthalene. KARL FLEISCHER and GREGOR FELDMEIER (*Ber.*, 1922, 55, [B], 3290—3293).—A solution of 1-methyl-5:6:7:8-tetrahydronaphthalene in carbon disulphide is converted by chromyl chloride dissolved in the same solvent at 0° into a chocolate-brown additive compound which is decomposed by ice-cold water with the production of small quantities of 5:6:7:8-tetrahydronaphthalene-1-aldehyde, a colourless liquid, b. p. $130-140^{\circ}$ (mainly 135°)/18 mm., which gives a colourless, crystalline product with sodium hydrogen sulphite. Similarly, 2-methyl-5:6:7:8-tetrahydronaphthalene gives 5:6:7:8-tetrahydronaphthalene-2-aldehyde, a colourless, mobile liquid, b. p. $150-155^{\circ}$ /14 mm. The compound with sodium hydrogen sulphite and the *semicarbazone*, colourless needles, m. p. $221-223^{\circ}$, are described. Attempts to isolate an oxime or thiosemicarbazone or

to condense the aldehyde with aniline, *p*-nitroaniline, or phenylacetonitrile were unsuccessful.

H. W.

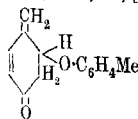
Preparation of *cyclo*Butanone by the Pyro-chemical Decomposition of 1-Hydroxycyclobutane-1-carboxylic Acid. N. J. DEMJANOV and MARIE DOJARENKO (*Ber.*, 1922, 55, [B], 2737—2742).—*cyclo*Butanone has previously been a very difficultly accessible substance, and only the semicarbazone among its derivatives has been examined. Its preparation by the pyrogenic decomposition of 1-hydroxycyclobutane-1-carboxylic acid is now recorded, the yield, according to preliminary experiments, being about 15% of that theoretically possible.

1-Bromocyclobutane-1-carboxylic acid is converted into a mixture of 1-hydroxycyclobutane-1-carboxylic acid and its anhydrides by treatment with the calculated quantity of potassium carbonate in boiling, concentrated aqueous solution (cf. Perkin, T., 1892, 61, 42); the yield is 94%. Decomposition of the mixture occurs mainly at 280—300°, with the production of a mixture of carbon monoxide and carbon dioxide, and an acidic distillate containing *cyclo*butanone. The latter is purified through its semicarbazone, m. p. 212° (decomp.), or bisulphite compound. It condenses with benzaldehyde in aqueous-alcoholic solution in the presence of potassium hydroxide to form *dibenzylidenecyclobutanone*, $C_{18}H_{14}O$, leaflets, m. p. 170—171°.

The *anhydrides* formed during the preparation of 1-hydroxycyclobutane-1-carboxylic acid or remaining in the residue when it is distilled under reduced pressure have been further examined. One of these is crystalline and freely soluble in organic media; it has m. p. 65°. Its molecular weight in boiling ether is in agreement with the formula $C_{10}H_{12}O_4$, whereas in freezing benzene it appears to have the composition $(C_{10}H_{12}O_4)_2$. Other anhydrides do not crystallise and are insoluble in all the usual media. They decompose when heated into carbon monoxide and *cyclo*butanone. They are remarkably stable towards water, by which, however, they are decomposed at 150—160°. Analyses are in agreement with the formula $C_{20}H_{26}O_8$ ($= 4C_5H_8O_2 - 3H_2O$); the molecular complexity is probably much greater, but it could not be determined on account of the insolubility of the substances. H. W.

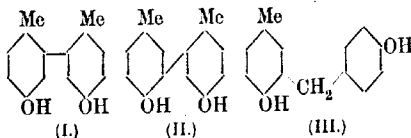
Action of the Chlorides of Phosphorus on Chlorodimethyl-dihydroresorcinol. LEONARD ERIC HINKEL and WILLIAM DUDLEY WILLIAMS (*T.*, 1922, 121, 2498—2502).

Oxidation of Phenols. VII. Dehydrogenation of *p*-Cresol. RUDOLF PUMMERER, DONA MELAMED, and HANS PUTTFARCKEN (*Ber.*, 1922, 55, [B], 3116—3132; cf. A., 1914, i, 714; 1915, i, 417; 1919, i, 439, 440, 442).—The oxidation of *p*-cresol does not appear to take place in the same manner as that of α -methyl- β -naphthol. The main product is an unsaturated monoketone, the properties of which are in accord with the conception that it is 2-*p*-tolyl-oxy-2:3-dihydro-*p*-benzoquinomethane (anneked formula).



A solution of *p*-cresol in aqueous sodium carbonate is gradually treated with a saturated solution of potassium ferricyanide at 0°; the product which separates is filtered and purified by fractional distillation under diminished pressure, whereby there are obtained unchanged *p*-cresol, 2-*p*-tolyl-oxy-2:3-dihydro-*p*-benzoquinomethane, 3:3'-di-*p*-cresol, colourless needles, m. p. 154°, and a dihydroxy-phenol, $C_{14}H_{14}O_2$, m. p. 194°, which is identical with the product isolated by Fichter and Ackermann (A., 1919, i, 586) by the anodic oxidation of *p*-cresol (the latter authors erroneously attributed to it the formula $C_{14}H_{14}O_3$); the substance crystallises with one molecular proportion of ethyl or methyl alcohol, which is removed with considerable difficulty. The corresponding diacetate has m. p. 108° (Fichter gives 111°). 2-*p*-Tolyl-oxy-2:3-dihydro-*p*-benzoquinomethane (see above) crystallises in colourless leaflets, m. p. 124.5°. Its molecular weight in freezing benzene is in harmony with the formula $C_{14}H_{14}O_2$. It is insoluble in cold sodium hydroxide solution, but is somewhat dissolved by the warm solution. Concentrated alcoholic potassium hydroxide solution dissolves it completely, but it separates unchanged after addition of water. It is slowly converted by sodium wire in the presence of anhydrous ether into a yellow sodium salt which is transformed by benzoyl chloride into the *monobenzoyl* derivative, $C_{21}H_{18}O_3$, colourless crystals, m. p. 153—154°. Its reluctance to pass into an enolic form is evidenced by its inability to react with boiling benzoyl chloride, acetyl chloride and pyridine, or phenylcarbimide. The presence of enol in its alcoholic solution cannot be detected by titration with bromine. It couples with *p*-nitrobenzenediazonium hydroxide in alcoholic solution, and slowly dissolves in boiling sodium hydrogen sulphite solution, with the production of sulphonic acid in place of a normal bisulphite compound. It is coloured bright red by perchloric acid. It yields an *oxime*, $C_{14}H_{15}O_2N$, colourless plates, m. p. 203—204°, a *phenylhydrazon*, $C_{20}H_{20}ON_2$, long, colourless needles, m. p. 181—182° after becoming brown at 170° (in an atmosphere of carbon dioxide) and *semicarbazone*, $C_{15}H_{17}O_2N_3$, colourless leaflets, m. p. 249—251 (decomp.).

The ketone is transformed by the protracted action of cold strong mineral acids into a *dihydroxyphenol*, $C_{14}H_{14}O_2$, needle m. p. 158°, which is characterised by conversion into the corresponding *dimethyl ether*, $C_{14}H_{12}(OMe)_2$, coarse, glassy prisms, m. p. 86°. Three of the



possible dihydroxyphenols, $C_{14}H_{14}O_2$, are known; the substance under investigation is not identical with any of these so that the choice of its constitution lies between the three remaining (annexed) formulæ.

If the ketone has the constitution assigned to it, it might be expected to be readily transformable into 2-*p*'-tolyl-oxy-*p*-cresol.

(annexed formula), This change has not yet been accomplished.

2-*p'*-Tolyl-*oxy-p-cresol*, m. p. 33—34°, has, however, been prepared synthetically by heating sodium *p*-tolyl-*oxy-p-cresol* (m. p. 54—55°, prepared from 2-amino-*p*-cresol). It gives a *phenylurethane*, $C_{21}H_{19}O_3N$, slender needles, m. p. 137—137.5°. The isomeric, 3-*p'*-tolyl-

oxy-p-cresol, coarse, colourless needles resembling asbestos, m. p. 35—37°, is prepared from sodium *p*-tolyl-*oxide*, 3-chloro-*p*-cresol, and copper powder at 170—190°; it is converted by *m*-nitrobenzoyl chloride in the presence of pyridine at 70° into the corresponding *m*-nitrobenzoate, rhombic, bipyramidal, pseudotetragonal crystals, $a:b:c=0.97:1:0.46$, m. p. 80°. Potassium *p*-tolyl-*oxide* is transformed by *p*-nitrobenzyl chloride in the presence of boiling alcohol into *p*-tolyl *p'*-nitrobenzyl ether, $C_6H_4Me \cdot O \cdot CH_2 \cdot C_6H_4 \cdot NO_2$, long, pale yellow needles, m. p. 86—87°, which is reduced by a solution of stannous chloride and hydrogen chloride in glacial acetic acid at 0° to *p*-tolyl *p'*-aminobenzyl ether, m. p. 110° (the pale yellow *hydrochloride* is described). Attempts to convert the free base through its diazonium compound into *p*-tolyl *p'*-hydroxybenzyl ether were unsuccessful, but it is placed beyond doubt that the substance, m. p. 124° (see above), is not formed in this manner. H. W.

Synthesis of Fisetole. ADOLF SONN and SUSANNE FALKENHEIM (*Ber.*, 1922, 55, [B], 2975—2985).—A number of unsuccessful attempts to synthesise fisetole [ω -hydroxyresacetophenone] are described. The substance is finally obtained by the condensation of resorcinol with carbethoxy- or methylcarbonato-acetonitrile; fission of the ketimide hydrochloride thus produced and elimination of the carbalkoxy-group.

2-Acetoxy 5-methoxycoumaranone, $OMe \cdot C_6H_3 \cdot \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ C(OAc) \end{smallmatrix} > CH$, nearly leaflets, m. p. 62°, is prepared by the action of acetic anhydride and anhydrous sodium acetate on methoxycoumaranone.

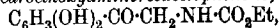
2:4-Dimethoxyphenyl bromomethyl ketone, $C_6H_3(OMe)_2 \cdot CO \cdot CH_2Br$, colourless crystals, m. p. 101—102°, after previous softening, is obtained by the action of hydrogen bromide on a solution of bromoacetonitrile and resorcinyl dimethyl ether in anhydrous ether in the presence of zinc chloride and decomposition of the primary product with boiling water.

2:4-Dihydroxyphenyl bromomethyl ketone, slender, colourless needles, m. p. 127° after previous softening, is prepared in a similar manner; it is converted by acetic anhydride in the presence of a little concentrated sulphuric acid into the corresponding diacetate, quadratic prisms, m. p. 76°, whereas acetic anhydride and sodium acetate transform it mainly into the diacetate of 5-hydroxycoumaranone, m. p. 157°, and a substance, m. p. 118° (m. p. of corresponding de-acetylated product, 257°) which has not been investigated closely, but appears to be derived by the condensation of two molecules of ω -bromoresacetophenone.

2:4-Dihydroxyphenyl iodomethyl ketone, $C_6H_3(OH)_2 \cdot CO \cdot CH_2I$, long

flattened prisms, m. p. 141° , after previous softening to a red liquid, is prepared by the action of sodium iodide on the corresponding ω -chloro-compound dissolved in anhydrous acetone; the diacetate crystallises in coarse, flattened prisms, m. p. 97° . *4-Hydroxy-2-methoxyphenyl iodomethyl ketone*, obtained in a similar manner to the preceding compound, forms needles, m. p. 128° , after previous softening.

Phthalimidoacetonitrile, $C_6H_4(CO)_2 \cdot N \cdot CH_2 \cdot CN$, almost colourless, thin leaflets, m. p. $124-125^{\circ}$ after previous softening (prepared from chloroacetonitrile and potassium phthalimide at 140°), could not be caused to condense with resorcinol in the desired manner. *ω -Benzoylaminoresacetophenone*, $C_6H_5(OH)_2 \cdot CO \cdot CH_2 \cdot NHBz$, oblique prisms, m. p. 255° (decomp.) after darkening and softening at 252° (prepared smoothly by the Hoesch reaction from resorcinol and hippuryl cyanide), did not prove a convenient source of ω -aminoresacetophenone, since elimination of the benzoyl group could not be effected readily. The latter substance [as hydrochloride, decomp. 257° (cf. Tutin, T., 1910, 97, 2512)] is, however, smoothly prepared by condensing resorcinol with carbethoxyaminoacetonitrile to form *ω -carbethoxyaminoresacetophenone*,



needles, m. p. $156-157^{\circ}$ after previous darkening and heating the carbethoxy-compound with hydrochloric acid (1 : 1).

Ethylcarbonatoacetonitrile, $CN \cdot CH_2 \cdot O \cdot CO_2Et$, a colourless, mobile liquid, b. p. $127^{\circ}/50$ mm., is obtained by the interaction of glycolonitrile and ethyl chloroformate in the presence of benzene and dimethylaniline; *methylcarbonatoacetonitrile* has b. p. $116-118^{\circ}/46$ mm. The ethyl ester condenses with resorcinol in ethereal solution in the presence of hydrogen chloride and zinc chloride to yield a ketimide hydrochloride which is decomposed by boiling water into *ω -ethylcarbonatoresacetophenone*, $C_6H_5(OH)_2 \cdot CO \cdot CH_2 \cdot O \cdot CO_2Et$, colourless, rectangular plates, m. p. $104-105^{\circ}$, to a turbid liquid which becomes clear at 107° ; the corresponding methyl compound crystallises in long, colourless needles, m. p. $157-158^{\circ}$. The esters are hydrolysed by 2*N*-sodium hydroxide solution at the atmospheric temperature to fisetole, m. p. 189° after previous softening and discoloration [*phenylhydrazone*, slender, pale yellow needles, m. p. 109° (decomp.)].

Ethylcarbonatoacetonitrile and resorcinyl dimethyl ether give the compound, $C_6H_3(OMe)_2 \cdot CO \cdot CH_2 \cdot O \cdot CO_2Et$, colourless, rectangular plates, m. p. $74-75^{\circ}$, from which 2 : 4-dimethoxyphenyl hydroxymethyl ketone is obtained. H. W.

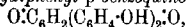
2 : 4-Dinitrobenzil. GERALD BISHOP and OSCAR LISLE BRADY (T., 1922, 121, 2364-2370).

The Addition of Benzene to *p*-Benzoquinone. RUDOLF PUMMERER and ERNST PRELL (*Ber.*, 1922, 55, [B], 3105-3116).—The addition of benzene to *p*-benzoquinone takes place at the atmospheric temperature with the production of 2 : 5-diphenyl-*p*-benzoquinone, yellow leaflets, m. p. 214° . The solution at first becomes intensely blue, owing to the formation of an additive compound of diphenylquinone and aluminium chloride, and then

brownish-black as the quinone is gradually reduced by the hydrogenating action of the benzene and aluminium chloride. Reaction appears to occur in accordance with the scheme: $\text{O}:\text{C}_6\text{H}_4:\text{O} + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5\text{Ph}(\text{OH})_2 \xrightarrow{-2\text{H}} \text{O}:\text{C}_6\text{H}_4:\text{O} + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5\text{Ph}_2(\text{OH})_2 \xrightarrow{-2\text{H}} \text{O}:\text{C}_6\text{H}_4:\text{O} + \text{C}_6\text{H}_6$. Under similar conditions, *p*-benzoquinone tetrachloride reacts very slowly; it is therefore considered that the primary product of the change is a mixed additive compound of aluminium chloride, *p*-benzobenzene, and quinone.

The derivatives of benzene react more readily and give better yields than the parent hydrocarbon. Thus, *p*-benzoquinone, toluene, and aluminium chloride at 0° give 2:5-di-*p*-tolylquinol, coarse prisms, m. p. 189° (corresponding *di*-acetate, m. p. 204°), which is oxidised by air in the presence of dilute aqueous sodium hydroxide solution to 2:5-di-*p*'-tolyl-*p*-benzoquinone, m. p. 220°. The latter substance exists in two modifications, red, monoclinic, prismatic crystals, $a:b:c :: 1.3035:1:1.7328$, $\beta=129^\circ 14\frac{1}{2}'$, which are obtained by crystallisation from ethyl acetate, and pale yellow, delicate leaflets which appear to belong to the triclinic system, but which are too ill-defined to permit crystallographical measurement; they are obtained by evaporation of a solution of the substance in benzene. The red modification is obtained when the yellow form is warmed on the water-bath and is stable in the dark; on exposure to light it becomes covered with a superficial layer of the yellow form. The case appears to be one of dimorphism. The action of toluene and aluminium chloride on *p*-benzoquinone in the presence of hydrogen chloride leads to the formation of ditolylquinol, m. p. 187–188°, and the *quinhydrone* of 2:5-di-*p*-tolylquinone.

2:5-*p*:*p*'-Dihydroxydiphenyl-*p*-benzoquinone,



small, brownish-red needles, m. p. above 327° after softening and blackening at about 287°, is prepared by the gradual addition of a solution of phenol in carbon disulphide to a mixture of the latter with *p*-benzoquinone and finely divided aluminium chloride at 0°. The corresponding *di*-acetate, $\text{O}:\text{C}_6\text{H}_2(\text{C}_6\text{H}_4\text{OAc})_2:\text{O}$, crystallises in aggregates of small prisms, decomp. 260° after softening at 243°. A solution of the quinone in rectified spirit is reduced by stannous chloride and hydrogen chloride to 2:5-di-*pp*'-dihydroxyphenylquinol, $\text{C}_6\text{H}_2(\text{OH})_2(\text{C}_6\text{H}_4\text{OH})_2$, pearly leaflets or small needles, m. p. 303°, which is transformed by sodium acetate and acetic anhydride into the corresponding *tetra*-acetate, a colourless, crystalline powder, m. p. 250°.

Di-*p*'-anisyl-*p*-benzoquinone, long, orange-red needles, m. p. 231°, is prepared from *p*-benzoquinone, anisole, and aluminium chloride in the presence of carbon disulphide at 0°. It is reduced by stannous chloride to 2:5-di-*p*-anisylquinol, greyish-white leaflets, m. p. 203°.

H. W.

Hydroxynaphthaquinones. V. Derivatives of 2-Bromo-5-hydroxy-1:4-naphthaquinone (Monobromojuglone). ALVIN S. WHEELER and B. NAIMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 2331–2334)*.—Monobromojuglone (2-bromo-5-hydroxy-1:4-naphthaquin-

one) (cf. Wheeler and Scott, A., 1919, i, 490) is best prepared by suspending juglone in glacial acetic acid and shaking the suspension with bromine for fifteen minutes. The dibromide so formed is separated by pouring the mixture into water, and is then boiled with absolute alcohol, when 2-bromojuglone is obtained. This compound gives a *benzoate*, m. p. 222°, and in alcoholic solution with dry hydrogen chloride is converted into 2-chlorojuglone, which also gives a *benzoate*, m. p. 222°. On bromination in hot glacial acetic acid, 2-bromojuglone yields 2:3-dibromo-5-hydroxy-1:4-naphthaquinone, m. p. 169°, which gives an *acetate*, m. p. 172°, and by treatment with dry hydrogen chloride in absolute alcohol is converted into 2:3-dichloro-5-hydroxy-1:4-naphthaquinone, m. p. 153° (cf. Wheeler and Scott, *loc. cit.*). When warmed with alcoholic sodium hydroxide, dibromojuglone is converted into a *bromodihydroxynaphthaquinone*, in which the bromine atom in position 2 probably remains. This compound is obtained in a yellow form, m. p. 192°, which is anhydrous, and in a red form which contains 1H₂O. W. G.

1-Hydroxylaminoanthraquinone and some of its Derivatives. WALTER H. BEISLER and LAUDER W. JONES (*J. Amer. Chem. Soc.*, 1922, 44, 2296—2306).—1-Nitroanthraquinone is best prepared by warming anthraquinone with fuming nitric acid (d 1.60) and crystallising the crude product successively from glacial acetic acid, toluene, and acetone. So prepared, it has m. p. 232.5—233.5° (corr.), which is much higher than that usually given in the literature (cf. Barnett, "Anthracene and Anthraquinone," 1922). The amino-compound, prepared by reduction with potassium sulphide, has m. p. 252—253° (corr.). When the nitro-compound is reduced in pyridine solution by hydrogen sulphide, it yields 1-hydroxylaminoanthraquinone, which gives an unstable *potassium* salt. The hydroxylamino-compound gives a sulphonic acid derivative which dyes wool and silk without a mordant. It gives a deep bluish-green solution in alkalis, and from such solutions can be precipitated unchanged if the solution is not exposed to air. It is a fairly strong reducing agent, and is remarkably stable to aldehydes. It reacts with diazobenzene in alkaline solution, giving a reddish-brown powder, m. p. 140° (decomp.), and gives a *carbamido-derivative*, m. p. 236°. When air is bubbled through its solution in sodium hydroxide, 1-nitrosoanthraquinone, m. p. 223—224°, is obtained. W. G.

The Acenaphthene Series. II. FRITZ MAYER and HEINRICH SCHÖNFELDER (*Ber.*, 1922, 55, [B], 2972—2974; cf. A., 1920, i, 301).—It has been shown previously (*loc. cit.*) that the direct bromination of acenaphthenequinone does not give a uniform product. It is now found that naphthalic anhydride is produced by the action of bromine on acenaphthenequinone dissolved in nitrobenzene at 200°. The reaction is not shown by bromine or by nitrobenzene separately, or by bromine in the presence of other solvents, such as chlorobenzene.

-Ciba-red, obtained by the bromination of Ciba-scarlet-G-1, is

shown to contain the bromine atom in the acenaphthene nucleus, since when it is boiled with alcoholic potassium hydroxide solution it is converted into thiosalicyclic acid and 5(or 6)-bromo-1-*keto*-2-aldehydoacenaphthene, greenish-brown needles, m. p. 255°. The corresponding, *anil* crystallises in orange-red needles, m. p. 175°, whilst the *phenylhydrazone* forms yellow needles, m. p. 193° (decomp.). The aldehyde is oxidised by sodium dichromate in the presence of glacial acetic acid to 4-bromonaphthalic anhydride, m. p. 215°.

H. W.

The Camphenilone Group. III. The Homogeneity of *apoBornylene*. *apoCyclene*, a New Tricyclic Hydrocarbon.

GUST. KOMPPA and R. H. ROSCHIER (*Annalen*, 1922, 429, 175—190).—In continuation of the experiments of Hintikka and Komppa (A., 1912, i, 278), it is found that the ozonide, $C_9H_{14}O_3$ (now described as a solid), m. p. 55°, decomp., obtained from *apobornylene*, is not formed in theoretical yield. The reason is that *apobornylene* prepared from camphenilone dichloride contains 20—30% of an isomeric hydrocarbon *apocyclene* (annexed formula), m. p. 42.5—43°, b. p. 138—139°, d_4^{20} 0.8710, n_D^{20} 1.45144, which is the chief product in the hydrocarbon mixture obtained by heating *methyl camphenilylzanthane*, b. p. 147°/8 mm.



The constitution assigned to *apocyclene* receives support from the reaction with acetic acid and sulphuric acid which bring about fission at the point indicated by the dotted line in the formula, the product being β -fenchocamphoryl acetate, b. p. 81—82°/8 mm. This is readily hydrolysed to β -fenchocamphorol, which can be identified by oxidation to r - β -fenchocamphorone or to *apofencho*-camphoric acid.

C. K. I.

Essential Oils from Tonkin and Annam. JEAN GATTE-FOSSE (*La Parfumerie moderne*, 1922, 15, 89—90; from *Chem. Zentr.*, 1922, iii, 502—503).—Star anise oil from the fruits and flowers of *Illicium verum* has d_4^{25} 0.983; α_D $-0^\circ 8'$; n_D^{20} 1.5546; ester number, 9.33; acetyl number, 42.93; solidification point, 9°; m. p. 13.5°. Pomelunus oil from *Citrus decumana*, obtained by distillation, has d_4^{15} 0.853; α_D $+97^\circ$; n_D^{20} 1.4742; ester number, 13.62; acetyl number, 44.23; citral content, 26% (?). Basilium oil has d_4^{20} 0.936; α_D $+4^\circ 8'$; n_D^{20} 1.4942; ester number, 20.9; acetyl number, 111.06. Camphor oil from young branches has d_4^{15} 0.936; n_D^{20} 1.4704; ester number, 15.67; acetyl number, 64.21. Essential oil from *Litsaea citrata* (May-chang oil) has d_4^{20} 0.866; α_D $+20^\circ 2'$; n_D^{20} 1.4620; ester number, 7.65; acetyl number, 153.07; citral content, 8.15%. *Cathetus fasciculata* yields a yellow essential oil having d_4^{15} 0.885; α_D $-6^\circ 5'$; n_D^{20} 1.4790; ester number, 7.47; acetyl number, 53.20; aldehyde content, 5.2%; also a green oil having d_4^{20} 0.886; α_D $-0^\circ 6'$; n_D^{20} 1.4772; ester number, 10.45; acetyl number, 50.21. Beu-ring oil from the leaves of *Alpinia* or *Zingiber*, sp., has a pleasant tar-like odour; d_4^{15} 0.902; α_D $+8^\circ 8'$; n_D^{20} 1.4884; ester number, 10.92; acetyl

number, 123-57. Sau-mon oil from *Cunninghamia sinensis*, has a strong odour like terpineol, d^{15}_4 0.957; α_D $-23^\circ 6'$; n_D^{20} 1.4932; ester number, 21.09; acetyl number, 120.02. Pe-mon oil from *Fokienia hodginsii* has d^{15}_4 0.913; α_D $+13^\circ$; ester number, 23.14; acetyl number, 188.34.
 . . G. W. R.

Relation between Ability to form Resins and Chemical Constitution. III. A New Method for producing Synthetic Resins. W. HERZOG and J. KREIDL (*Z. angew. Chem.*, 1922, 35, 641-643).—The preparation of a number of synthetic resins is described in which organic substances containing the group $-\text{CO}-\text{CH}=\text{CH}-$ are heated to temperatures of between 200° and 240° in a stream of carbon dioxide for from two to twelve hours. Resins can also be obtained from substances containing the above group as part of a cyclic ring. Such a substance is 1-keto-2-cinnamylidenetetrahydronaphthalene, $\text{C}_{10}\text{H}_8\text{O}:\text{CH}=\text{CH}:\text{CHPh}$, prepared by heating α -ketotetrahydronaphthalene (7.5 grams) and cinnamaldehyde (7 grams) in 15 c.c. of alcohol with a few drops of concentrated sodium hydroxide. It crystallises from methyl alcohol in large yellow leaves (m. p. $132-134^\circ$), and dissolves in concentrated sulphuric acid, giving a yellowish-red colour. All polymerisations of organic substances to resins are ascribed to the presence of the group $-\text{CO}-\text{CH}=\text{CH}-$.
 H. C. R.

Rhinanthin and Aucubin. Rhinanthin is Impure Aucubin. MARC BRIDEL and (Mlle) MARIE BRAECKE (*Compt. rend.*, 1922, 175, 640-643).—Three analyses of rhinanthin did not yield concordant results, the carbon content varying from 44 to 48%, and as its reactions are similar to those of aucubin, a comparison of the two substances was made. The results led to the conclusion that rhinanthin is a mixture of aucubin and sucrose. The authors consider that as the name "rhinanthin" no longer represents a distinct substance, it should be abandoned.
 H. J. E.

Saponins. VIII. The Saponins from the Leaves of *Aralia montana*, Bl. (Galacturonoid-Saponins and their Magnesium and Calcium Salts.) A. W. VAN DER HAAR (*Ber.*, 1922, 55, [B], 3041-3069).—The leaves of *Aralia montana*, Bl., are extracted successively with light petroleum and ether. The first extract (3.75% on the material taken) contains a trace of alkaloid, much chlorophyll, and a plant wax of which the alcoholic component is myricyl alcohol; the second extract (2%) contains chlorophyll, a trace of alkaloid, and a small amount of a tannin.

The powdered leaves and stems contain about 1.6% of saponins which are members of at least three groups. Free saponins are present in addition to their calcium and magnesium salts; these are precipitated by basic, but not by normal, lead acetate. The amount of the saponins appears to be variable. In the isolation of the saponins, it is necessary that the extraction with methyl alcohol (95%) should be followed by treatment with ethyl alcohol (45%), since otherwise the salts of the saponins remain undissolved. The saponins are poisonous towards fishes and exhibit hæmolytic

action; the magnesium salt is about three times as potent as the free saponin. The *aralia* saponins give the violet coloration with sulphuric acid which is characteristic of the other members of the class. The hydrolysis of the saponin can be effected only with very unusual difficulty. Proximate analysis and quantitative hydrolysis show the saponin to contain water, 4.8%; ash, 1.8%; *d*-galacturonic acid, 1.8%; pentoses [*L*-arabinose], 13.3%; methylpentoses, 2.1%; hexoses (*d*-galactose and dextrose), 16.15%; *d*-galactose, 2%, sapogenin, 56%. Analysis of the magnesium and calcium saponins gives: water, 7.2%; ash, 5.3%; *d*-galacturonic acid, 7.39%; arabinose, 8.64%; methylpentoses, 6.24%; dextrose, 5.6%; *d*-galactose, 3%; sapogenins, 31.2%. Other saccharides or acids are not present.

Araligenin, colourless needles, m. p. 275°, is readily isolated from the crude mixture of sapogenins. It can be sublimed. It separates from ethyl alcohol with alcohol of crystallisation which is variable in amount, and thus causes the m. p. 301°, 311°, and 273–274° to be observed. When dried at 150°, all these products give a substance which has the same specific rotation (+71° in a mixture of alcohol and pyridine) and identical composition. Araligenin dried at 150° is therefore to be regarded as a definite chemical individual. It has the composition $\text{OH}\cdot\text{C}_{25}\text{H}_{40}\cdot\text{CO}_2\text{H}$. It gives the Liebermann cholesterol reaction (violet \rightarrow blue \rightarrow green). It yields a *potassium* salt, $\text{C}_{25}\text{H}_{41}\text{O}_2\text{K}\cdot 2\text{H}_2\text{O}$, slender, colourless needles, which do not melt below 300°, a *methyl* ester (prepared by the action of methyl alcohol and methyl iodide or of methyl sulphate on sodium araligenin), m. p. 180° after softening at 120°, and a *monoacetyl methyl* ester, $\text{OAc}\cdot\text{C}_{25}\text{H}_{40}\cdot\text{CO}_2\text{Me}$, small, colourless needles, m. p. 217–218°. The methyl ester is not hydrolysed when heated during two hours with a 10% solution of potassium hydroxide in ethyl alcohol (50%), thus affording a very pronounced example of steric hindrance. The hydroxy-group of araligenin, in consequence of steric hindrance due to the proximity of the free carboxyl group, cannot be acetylated in the usual manner. The operation can, however, be effected smoothly after esterification of the carboxyl group.

Araligenin is converted into a mixture of terpene hydrocarbons, carbon dioxide, and water when distilled with zinc dust in an atmosphere of hydrogen. The hydrocarbons can be separated by distillation with steam into a light, volatile fraction which gives a violet coloration with a mixture of glacial acetic and sulphuric acids, and a non-volatile residue which gives a blue and subsequently a green colour with the mixture of acids. The volatile fraction has exactly the composition $(\text{C}_5\text{H}_8)_n$. The distillation of araligenin with zinc dust in an atmosphere of hydrogen is represented provisionally by the equation $\text{OH}\cdot\text{C}_{25}\text{H}_{40}\cdot\text{CO}_2\text{H} = (\text{C}_5\text{H}_8)_5 + \text{CO}_2 + \text{H}_2\text{O}$.
H. W.

Tannins and Similar Substances. II. Chinese Tannin.
KARL FREUDENBERG and WILHELM SCHLÄSI (*Ber.*, 1922, 55, [B], 2813–2816).—Doubts as to the homogeneity of Chinese tannin

have been strengthened by the observation of Iljin (A., 1914, i, 567) that it can be separated by repeated precipitation with zinc acetate into a fraction of high specific rotation in water ($[\alpha]_D +137.85^\circ$ and one of low optical activity ($[\alpha]_D +5.16^\circ$). A repetition of Iljin's experiments with commercial tannin and with the product obtained by the authors themselves from Chinese galls has confirmed the accuracy of his observations and has also shown that the specific rotations of the fractions, although differing so widely in aqueous solution, are identical when they are dissolved in formamide, acetone, alcohol, glacial acetic acid, or pyridine. An explanation of the apparent anomaly is found in the fact that the tannin forms a colloidal solution only in water, in which, therefore, the magnitude of the specific rotation depends greatly on the degree of dispersivity of the particles; this is greatly influenced by the presence of minute quantities of impurity, which are gradually removed by precipitation in Iljin's experiments, and can also be coagulated and rendered insoluble in ethyl acetate by heating the tannin at 100° . Chinese tannin may be regarded as fundamentally homogeneous.

Highly active specimens of the tannin are prepared in the following manner. The galls are extracted with cold water, and the extract, after being neutralised with sodium carbonate, is treated with ethyl acetate; the product obtained after removal of the solvent has $[\alpha]_D +90^\circ$ in aqueous solution (3%), and the specific rotation is nearly independent of the concentration. Attempts to obtain a more active substance by the use of inorganic adsorbents (kaolin, etc.) or organic precipitants (starch, albumin, casein) were unsuccessful. If, however, the product is dried in a vacuum at 100° , and subsequently treated with anhydrous ethyl acetate, a small amount of highly coloured material remains undissolved, and the activity of the dissolved portion is increased to $+116^\circ$ in water (1%). Two further treatments in the same manner give a product which is completely soluble in ethyl acetate, and has the constant specific rotation $[\alpha]_D +138^\circ$ in aqueous solution (1.5%).

H. W.

The Formation of Melanin from Organic Substances.

O. ADLER and W. WIECHOWSKI (*Ber.*, 1922, 55, [B], 3030—3038; cf. this vol., i, 498).—The ability of a very large number of organic substances to form melanin acids has been examined in the following manner. The material under investigation (1—2 dg.) is dissolved or suspended in water (10—12 c.c.) and 3—4 drops of *N*-ferrie chloride solution are added. The solution is divided into two parts, of which one serves as a control. Hydrogen peroxide (3%, 0.2—0.5 c.c.) is added to the other portion. If the substance is capable of producing melanin acids, a dark, sometimes almost black, coloration is developed after short heating, or sometimes even at the atmospheric temperature. Protracted heating is to be avoided, as the melanin acids are readily oxidised further to colourless substances. The dark mixture is rendered alkaline with sodium hydroxide when the melanin acid dissolves or remains

dissolved, as the case may be. The test must be performed in neutral or faintly acid solution.

Under the described conditions, melanin acids are only produced from cyclic substances. Compounds belonging to the terpene, triphenylmethane, phenanthrene, anthracene, and pyridine groups exhibit little or no tendency towards the formation of melanin acids. Very marked ability is exhibited by the aniline group, phenylhydrazine, and its substitution products, phenols, quinone, aromatic monoaldehydes and ketones, aromatic monocarboxylic and phenolmonocarboxylic acids and aromatic amino-acids. A positive reaction is given by *p*-diphenol, benzidine, and tolidine, but scarcely by dianisidine. Naphthalene does not yield melanin acids, which are yielded by the naphthols and naphthylamines. Among heterocyclic compounds, thiophenic acid, pyrrole, coumarone, indole, and tryptophan give melanin acids. Quinoline hydrochloride and the hydroxyquinolines give a faintly and strongly positive action respectively. Positive results are also given by isoquinoline, acridine, and the representatives of the tropine, cinchonine, and morphine groups.

The entrance of halogen into the nucleus diminishes or abolishes the tendency towards the formation of melanin acids, whereas the sulphonic group has no restrictive action. Aromatic arsenic compounds of the arsenic acid type have only a slight or no ability to produce melanin acids, even when they are derived from substances which are intensely active in this respect. The presence of an amino-group on the nucleus strengthens the ability of a substance to give melanin acids; the nitro-group does not exert a restrictive influence. The intensity of the melanin reaction is restricted, or production of melanin acids is entirely prevented, by the presence of methyl residues attached to the benzene nucleus. The effect of ester or ethereal groups depends to some extent on their more or less ready removal or decomposability under the influence of the oxidising mixture. As far as has been examined, the action of methyl and ethyl esters and methyl ethers of substances which themselves give the melanin reaction is positive. On the other hand, a negative reaction is observed when a cyclic residue is involved in the formation of the ester or ether (for example, phenyl salicylate, guaiacyl cinnamate), or when an inorganic component is present (guaiacyl carbonate, triguaiacyl phosphate).
H. W.

Pyranhydrones. III. The Constitution of Diarylmethylpyrylium Compounds. WILHELM SCHNEIDER and ALBERT ROSS (*Ber.*, 1922, 55, [B], 2775—2782; cf. Schneider and Meyer, A., 1921, i, 680; Schneider and Seebach, A., 1921, i, 877).—The compound obtained by the action of acetic anhydride and sublimed ferric chloride on a mixture of acetophenone and benzaldehyde has been regarded by Diltney (A., 1916, i, 829) as a 2:6-diphenyl-4-methylpyrylium salt. This view has been shared by Schneider and Seebach (*loc. cit.*),* who obtained the corresponding sulphoacetate by the action of sulphoacetic acid and acetic anhydride

on acetophenone. It is now found, however, that the same sulphoacetate is prepared by the action of acetic anhydride and sulphoacetic acid on dyponone, and since the product in this instance must necessarily be 4:6-diphenyl-2-methylpyrylium sulphoacetate, it follows that the compounds described previously must also be 4:6-diaryl-2-methylpyrylium compounds. Apparently acetophenone is first transformed into dyponone in the presence of either ferric chloride or sulphoacetic acid as catalyst, and this is then condensed with the acetic anhydride to give a pyrylium salt. Further confirmation of this view is found in the observation that ω -ethylideneacetophenone and acetophenone react in the presence of acetic anhydride and sublimed ferric chloride to give undoubtedly 2:6-diphenyl-4-methylpyrylium compounds which differ from those described previously.

The formula for the bluish-violet pyranhydrones must therefore be so amended that in their molecular complex a molecule of a benzenoid 4:6-diaryl-2-methyloxonium base is loosely united with an ortho-quinonoid 2-methylenpyran.

Dyponone is transformed by acetic anhydride and sulphoacetic acid into 4:6-diphenyl-2-methylpyrylium sulphoacetate, pale yellow needles, m. p. 204°; the corresponding iodide forms red crystals, m. p. 222°.

The additive compound of 2:6-diphenyl-4-methylpyrylium chloride and ferric chloride, a brownish-yellow salt, m. p. 205.5°, is prepared by the action of sublimed ferric chloride on phenyl propenyl ketone and acetophenone in the presence of acetic anhydride. 2:6-Diphenyl-4-methylpyrylium bromide crystallises in yellow, prismatic needles; it becomes carbonised but does not melt when heated; the corresponding iodide forms orange-red needles, decomp. above 240°, whereas the perchlorate crystallises in slender, lemon-yellow needles, m. p. 273° (decomp.). Addition of sodium acetate solution to 2:6-diphenyl-4-methylpyrylium bromide in faintly acid solution results in the formation of a dull red, amorphous precipitate, m. p. (indefinite) 155–160° after shrinking at 70° and darkening above 95°; the substance appears to be a pyranhydron.

H. W.

Preparation of Thionaphthensulphonic Acid. GSELL-SCHAFF FÜR TEERVERWERTUNG M. B. H. and RUDOLF WEISSEBERGER (D.R.-P. 353932; from *Chem. Zentr.*, 1922, iv, 499).—In the sulphonation of thionaphthen, the reaction is conducted in the presence of sufficient acetic anhydride to combine with all the water present in the sulphuric acid used, and formed in the reaction. The free acid is a viscid mass, crystallisable with difficulty. The potassium salt forms colourless platelets. The acid decomposes when heated at 140° with dilute sulphuric acid, forming thionaphthen and sulphuric acid.

G. W. R.

Preparation of Nortropinone and its Derivatives. E. MERCK, OTTO WOLFES, and HORST MAEDER (Brit. Pat. 177807; from *Chem. Zentr.*, 1922, iv, 439).— $\alpha\delta$ -Dialdehydes or $\alpha\delta$ -diketones are condensed with ammonia or primary amines and an acetone

derivative. For example, succinaldehyde is allowed to react with the dipotassium derivative of ethyl acetonedicarboxylate, ammonia, and ammonium chloride in aqueous solution. *Ethyl nortropinonecarboxylate* is obtained. It forms a *picrate* and a *methiodide*. The condensation product from succinaldehyde, benzylamine, and the dipotassium derivative of ethyl acetonedicarboxylate gives the enol reaction with ferric chloride. By heating with dilute sulphuric acid, *N-benzylnortropinone* is obtained, which yields a *dibenzylidene* compound. Condensation of succinaldehyde with glycine hydrochloride and calcium acetonedicarboxylate yields a product which does not give the enol reaction and gives a *dibenzylidene* derivative with benzaldehyde. Malealdehyde diacetate is shaken with 0.1N-sulphuric acid, neutralised with calcium carbonate, and condensed with methylamine and the dipotassium derivative of ethyl acetonedicarboxylate. The *monocarboxylic* ester formed (annexed formula) gives, on reduction, *ethyl tropinonecarboxylate*. An *homologous* ester of tropinonecarboxylic acid is obtained by condensation of acetonylacetone with the dipotassium salt of ethyl acetonedicarboxylate, methylamine, and methylamine hydrochloride in aqueous solution.

G. W. R.

Preparation of Tropinecarboxylic Acid. E. MERCK, OTTO WOLFE, and HORST MAEDER (D.R.-P. 354696; from *Chem. Zentr.*, 1922, iv, 438).—A mixture of acetonedicarboxylic acid, methylamine, and succinaldehyde is reduced in the cold in neutral, slightly acid, or slightly alkaline solution. For example, a mixture of calcium acetonedicarboxylate, succinaldehyde, and methylamine is acidified with acetic acid and reduced with 3% sodium amalgam, the reaction of the mixture being maintained acid by addition of acetic acid. After addition of dilute sulphuric acid and removal of calcium sulphate by filtration, the filtrate is concentrated and treated with potassium hydroxide. The tropine bases are then extracted with ether. The neutralised alkaline solution is concentrated, and shaken with methyl alcohol. The methyl-alcoholic solution, after being freed from salts, contains *tropinecarboxylic acid* in the form of several optically inactive isomerides which are separable with difficulty. One of them is *ecgonine* (Willstätter and Bode, A., 1903, i, 36), from which the *methyl* ester, m. p. 122–126°, can be obtained. The benzoyl derivative, $C_{17}H_{21}O_4N$, m. p. 79–80°, is identical with optically inactive cocaine. G. W. R.

Preparation of Tropinonedicarboxylic Esters. E. MERCK, OTTO WOLFE, and HORST MAEDER (D.R.-P. 354950; from *Chem. Zentr.*, 1922, iv, 438–439).—Succinaldehyde is condensed in alkaline solution with acetonedicarboxylic acid and methylamine and the products of reaction are separated without saponification. For example, solutions of succinaldehyde in water, ethyl acetonedicarboxylate in ethyl alcohol, and methylamine and potassium hydroxide in water are mixed with careful cooling. After several hours, the products of reactions are neutralised with acid. After

evaporating off the alcohol, the residue is treated with ammonia and extracted several times with chloroform. After removal of the chloroform by distillation from the extract, *ethyl tropinone-dicarboxylate* remains as a viscid, uncrystallisable oil. It differs from the monocarboxylic ester in not forming a solid hydrate with water. Heating the ester with acids yields *tropinone*. The *monocarboxylic* ester is obtained by careful hydrolysis.

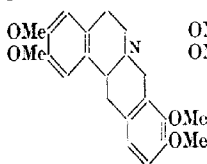
G. W. R.

The Resolution of Tropic Acid and the Stereochemical Configuration of the Cinchona Alkaloids. HAROLD KING and ALBERT DONALD PALMER (T., 1922, 121, 2577—2586).

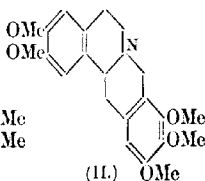
Preparation and Racemisation of Hyoscyamine and its Sulphate. A. GORIS and P. COSTY (Bull. Sci. Pharmacol., 1922, 29, 113—121; from Chem. Zentr., 1922, iii, 268—269).—Hyoscyamine and atropine may be separated by making use of their differing solubilities in cold light petroleum. Hyoscyamine in absolute ethyl alcohol has $[\alpha]_D -20.72^\circ$, in 50% ethyl alcohol, $[\alpha]_D -21.89^\circ$, in 20% ethyl alcohol, $[\alpha]_D -23.43^\circ$. The sulphates of hyoscyamine and atropine may be separated by their differing solubilities in ethyl alcohol. The transformation of hyoscyamine into atropine only proceeds to a small extent at 100° . It proceeds more rapidly when the hyoscyamine is dissolved in a little chloroform. At 118° , hyoscyamine is completely changed into atropine in two hours.

G. W. R.

Constitution of the Alkaloids of the Calumba Root. ERNST SPÄTH and KARL BÖHM (Ber., 1922, 55, [B], 2983—2995).—In a previous communication (Späth and Lang, this vol., i, 166), the



(I.)

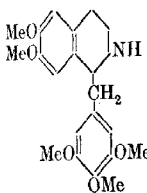


(II.)

annexed formula (I) has been assigned to palmatine. The other alkaloids of the calumba root, columbamine (Günzel, A., 1906, i, 976) and jatrorrhizine (Feist, A., 1908, i, 100) have been examined in detail by Feist, who has drawn the conclusion that they contain hydroxy- and methoxy-groups and, after complete methylation and hydrogenation, give the same final product (annexed formula II). Attempts are now described to prepare this compound synthetically, but as they are not completely successful, the alkaloids themselves have been subjected to re-examination. The isolation of columbamine and jatrorrhizine from calumba root is effected as described by the previous investigations, but doubts are expressed with regard to the homogeneity of the fractions which are soluble in potassium carbonate and potassium hydroxide, respectively. They have therefore been separately completely methylated and subsequently reduced. The observed melting points of the products are in agreement with those recorded by

Feist for columbamine methyl ether, jatrorrhizine dimethyl ether, and their hydro-compounds. The identity of the methylated products is also confirmed. On the other hand, it is shown both chemically and crystallographically that the substances are identical with palmatine and tetrahydropalmatine. The relationships of the various alkaloids of the calumba root appear therefore to be simpler than was expected. There are present, in addition to completely methylated palmatine, phenolic bases in which probably one or more of the methoxy-groups of palmatine are replaced by hydroxy-groups or by phenolic oxygen united to a readily eliminable complex.

The trimethyl ether of homogallic acid reacts with homoveratrylamine at 175° to yield *trimethylhomogalloylhomoveratrylamine*, $C_{21}H_{27}O_6N$, colourless needles, m. p. 98° , which is readily converted by phosphoryl chloride in the presence of boiling toluene into the corresponding *dihydroisoquinoline* derivative, an amorphous, glassy substance which is characterised in the form of its *picrate*, $C_{27}H_{28}O_{12}N_4$, yellow crystals, m. p. $154-155^{\circ}$. The substance is



reduced by tin and hydrochloric acid to 6:7-*dimethoxy-1-3':4':5'-trimethoxybenzyl-1:2:3:4-tetrahydroisoquinoline* (annexed formula), an amorphous solid which is characterised as its *N-m-nitrobenzoyl* compound (also amorphous) and *hydrochloride*, colourless needles. The subsequent condensation of this compound with methylal and hydrochloric acid does not proceed smoothly, yielding a crystalline compound, $C_{45}H_{54}O_{10}N_2$, m. p. 292° (decomp.), in an evacuated capillary and an amorphous substance, $C_{22}H_{25}O_5N$, which appears to be allied to tetrahydroberberine. By greatly diminishing the relative quantity of methylal and purifying the product of the reaction through the berberinium base, it was found possible to isolate a substance, $C_{22}H_{25}O_5N$, which might be identical with the pentamethoxy-compound (see above); it was, however, amorphous and certainly not identical with Feist's tetrahydrocolumbamine methyl ether.

H. W.

Strychnos Alkaloids. XXXIV. The Preparation of iso-Strychnine. HERMANN LEUCHS and RUDOLF NITSCHKE (*Ber.*, 1922, 55, [B], 3171-3174).—*iso*Strychnine has been obtained by Pictet and Bacovescu (*A.*, 1905, i, 815) by the action of water on strychnine at $160-180^{\circ}$. Attempts to repeat their work gave the substance in only 20-25% yield instead of 70-75% as recorded. More successful results were obtained by using a solution of ammonia in methyl alcohol. *iso*Strychnine, $C_{21}H_{22}O_2N_2 \cdot 3H_2O$, prismatic needles, has m. p. $223-224^{\circ}$ (particularly in an evacuated capillary) instead of $214-215^{\circ}$ as recorded. It dissolves in water at 100° to the extent of 1 part in 130-140 parts, and not 1 in 65. Contrary to Pictet and Bacovescu's observations, it is optically active, having $[\alpha]_D +24.1^{\circ}$ to $+25.1^{\circ}$ in alcohol and -39.47° to -41.0° in glacial acetic acid. It yields a well-crystallised *meth-*

iodide, $C_{22}H_{25}O_2N_2I \cdot H_2O$, colourless leaflets, m. p. about 223° (decomp.) after softening at 215° . The sulphonic acids obtained from it by means of manganese dioxide and sulphurous acid could not be caused to crystallise. It is readily oxidised by potassium permanganate in the presence of acetone, but characteristic acids, notably strychninonic acid or its dihydro-compound, could not be isolated; it is therefore improbable that strychnine and iso-strychnine are related in the same manner as fumaric and maleic acids.

H. W.

The Synthesis of Pyrrolidine. Reduction of Pyrrole by Catalytic Hydrogenation. N. J. PUTSCHIN (*Ber.*, 1922, **55**, [B], 2742—2748).—The catalytic hydrogenation of pyrrole in the presence of nickel at 200° (cf. Padoa, *A.*, 1906, i, 530) has been examined. The product is subjected to fractional distillation and the separate fractions are characterised by conversion into the hydrochlorides, platinichlorides, or picrates. The presence of diethylamine, methyl-*n*-propylamine, *n*-butylamine, *n*-amylamine, ethyl-*n*-propylamine, pyrrolidine, possibly 4-methylpiperidine, and (?) hexahydroindoline or α -*n*-butylpyrrolidine is established. It is remarkable that fission of the pyrrole ring must have occurred simultaneously at several different points in order to give the simpler compounds here described. The formation of amylamine and piperidine derivatives is explained by the primary condensation of two molecules of pyrrole followed by an extension of the hetero-five-membered to the hetero-six-membered ring.

The most advantageous method for the preparation of pyrrolidine is that due to Gabriel. Improved methods are described for the conversion of γ -chlorobutyronitrile by sodium phenoxide into γ -phenoxybutyronitrile and for the isolation of δ -phenoxy-*n*-butylamine by the reduction of the latter; during the change, *bis*- γ -phenoxy-*n*-butylamine, $(OPh \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO)_2NH$, lustrous plates, m. p. 162 — 163° , and γ -phenoxy-*n*-butyric acid, m. p. 59 — 5° , are also formed.

H. W.

The Action of Formaldehyde on Pyrrolidine and Piperidine. N. J. PUTSCHIN (*Ber.*, 1922, **55**, [B], 2749—2753).—Pyrrolidine is converted when heated with an equivalent amount of formaldehyde (as trioxymethylene) during six hours at 145 — 150° into 1-hydroxy-*γ*-methylpyrrolidine, $\begin{matrix} CH_2 \cdot CH_2 \\ | \quad | \\ CH_2 \cdot CH_2 \end{matrix} > N \cdot CH_2 \cdot OH$, 1:1'-methylenedi-pyrrol-

idine, $CH_2 \left(N < \begin{matrix} CH_2 \cdot CH_2 \\ | \quad | \\ CH_2 \cdot CH_2 \end{matrix} \right)_2$, and resinous substances. The substance first named is a yellow, viscous liquid, b. p. 55 — $56^\circ/30$ mm., which is hydrolysed by dilute hydrochloric acid to pyrrolidine hydrochloride and formaldehyde; the change takes place with such readiness at the atmospheric temperature that it is impossible to prepare the platinichloride, etc., the corresponding compound of pyrrolidine being obtained in its place. 1:1'-Methylenedi-pyrrolidine is a pale yellow liquid of low density, b. p. 94 — $95^\circ/30$ mm.; it has a marked tendency towards resinification, so that definite

salts can only be prepared with great difficulty. The brown, resinous residue left after the distillation is decomposed when heated into formaldehyde, pyrrolidine, and apparently an isomeric 1-hydroxymethylpyrrolidine, b. p. about 140° /atmospheric pressure. Under precisely similar conditions, piperidine is converted by trioxymethylene into a mixture of methylpiperidines, b. p. $33-35^{\circ}/35$ mm. (apparently 1- and 2-methylpiperidines), and 1:1'-methylenedipiperidine, b. p. $120-122^{\circ}/25$ mm., d_4^{20} 0.9371, d_4^{25} 0.9344, d_4^{30} 0.9335, n_D^{20} 1.4883 (the platinichloride was also prepared).

H. W.

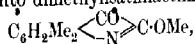
Condensation of Collidine with Acetaldehyde. HEIZABURŌ KONDŌ and TORIZŌ TAKAHASHI (*J. Pharm. Soc. Japan*, 1922, No. 487, 775-780).—When collidine (10 grams) is heated with paracetaldehyde (3.63 grams) in a sealed tube at 210° during fourteen hours, and the product fractionated under reduced pressure, 2:4-dimethyl-6-propenylpyridine (2 grams), a colourless oil, b. p. $110-111^{\circ}/12$ mm., is obtained. The constitution was proved by oxidation with 25% nitric acid, when 2:4-dimethylpyridine-6-carboxylic acid (Altar, A., 1887, 378) is formed. The aurichloride, yellow, rhombic plates, m. p. 135° ; the platinichloride, yellowish-brown, thin, rhombic plates, m. p. $205-206^{\circ}$; and the mercurichloride, colourless needles, m. p. $192-193^{\circ}$, were prepared. When reduced by Ladenburg's method, the base gives 2:4-dimethyl-6-propylpiperidine, a colourless liquid of slightly nicotine-like odour, b. p. 184° . The hydrochloride forms needles, m. p. $204-206^{\circ}$, the platinichloride, orange-yellow crystals, decomposing at 210° .

K. K.

Supposed Cases of Isomerism in the Isatin Series. A. HANTZSCH (*Ber.*, 1922, 55, [B], 3180-3194).—A further chapter in the controversy between Hantzsch and Heller concerning the existence of isomerides in the isatin series (cf. Heller, A., 1920, i, 766; 1921, i, 891; Heller and Benade, this vol., i, 582; Hantzsch, A., 1921, i, 597).

The existence of the bimolecular alkylisatoids is acknowledged and demonstrated by determinations of molecular weight, but the various derivatives are not so sharply distinguished from one another as Heller and Benade (*loc. cit.*) have supposed. The isomerism of the so-called "isatole" with isatin is disproved by Heller's determinations of the molecular weight. Its re-preparation has, however, been effected, and it is shown to be derived from a complex condensation product of isatin the constitution of which will be fully elucidated in a subsequent communication.

Heller's "dimethylisatin II" has been further investigated, since it is pointed out that its mode of production is exceptional in the series and the constitution ascribed to it is not consonant with its properties. Dimethylisatin silver is converted smoothly by methyl iodide at the laboratory temperature in the complete absence of moisture into dimethylisatinlactim ether,



m. p. 137°. The latter readily suffers hydrolysis in that one molecule of it becomes converted into the free lactim which condenses spontaneously with a second molecule of the ether to the so-called methylisatoid of the dimethylisatin series (annexed formula). The

direct production of this substance in Heller's experiments appears to be due to the use of an impure silver salt which only reacts at a higher temperature and to incomplete exclusion of moisture. Consequent on the non-existence of "dimethylisatin II," dimethylisatins III and IV also do not exist.

The author draws the general conclusion that isomerides of ordinary isatin and its substitution products do not exist. The substances which have been regarded as such are complex condensation products.

According to Heller, the reddish-violet silver salts of isatin and its derivatives which react readily with methyl iodide are to be regarded as *O*-salts, whereas the grey, indifferent compounds are *N*-salts. According to the author, all pure silver salts of the isatins are never grey except when they are contaminated by co-precipitated silver oxide. The grey salts are very readily formed from the more feebly acidic methylated isatins or solutions of their alkali salts by reason of their extensive hydrolysis.

[With WALTHER MEYER.]—An improved method for the production of 5:7-dimethylisatin is described in detail.

Pure silver salts of isatin and its derivatives are prepared by dissolving these substances in boiling alcohol and gradually adding a filtered aqueous solution of silver acetate (prepared from silver nitrate and sodium acetate). The precipitates are filtered, washed with alcohol (50%), and dried to constant weight at 100° or in a desiccator. The average yield is 60–70% of that theoretically possible. For their conversion into alkyl derivatives, the dry silver salt is moistened with anhydrous ether and treated with rather less than two molecular proportions of alkyl iodide. The mixture is placed in a desiccator shielded from light. The alkyl compounds are extracted with dry benzene in the absence of moisture and precipitated from the solutions by addition of light petroleum. The following compounds are thus prepared: isatin *O*-methyl ether, m. p. 101°; ethyl ether, m. p. 52°; *n*-propyl ether, m. p. 72°; isoamyl ether, m. p. about 40°; methyl ethers of 5-bromoisatin, m. p. 147°; 5-chloroisatin, m. p. 144°; 5-methylisatin, m. p. 134°; 5:7-dibromoisatin, m. p. 158°; 5:7-dimethylisatin, m. p. 137°. All the ethers are readily hydrolysed by aqueous alcohol to the original isatins. With the exception of the dibromo- (and probably also dichloro-) compounds they are hydrolysed by acetic acid or by atmospheric moisture to the isatoid monoalkyl ethers. The latter substances when rapidly heated darken at about 6–8° below their melting points, which are never definite, and at which total decomposition occurs. The following constants are recorded: isatoid monomethyl ether, $C_{17}H_{13}O_4N_2$, m. p. about

226°; ethyl ether, m. p. about 228°; propyl ether, m. p. about 189°; dimethylisatoid monomethyl ether, m. p. about 235°; tetramethylisatoid monomethyl ether, m. p. about 245°; dichloroisatoid monomethyl ether, m. p. about 239°; dibromoisatoid monomethyl ether, m. p. about 246°.

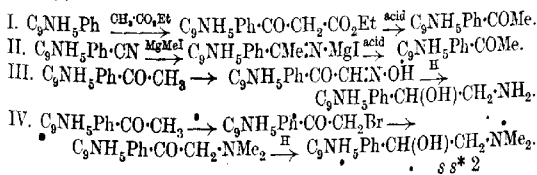
Isatindianil, $C_6H_4 \langle \begin{smallmatrix} C(NPh) \\ NH \end{smallmatrix} \rangle C(NPh)$, m. p. 210°, is readily obtained when a solution of the lactim ether (1 mol.) and aniline (2 mols.) in benzene is heated on the water-bath for about half an hour and the benzene as it evaporates is replaced by alcohol. It dissolves in alcoholic potassium hydroxide to a reddish-violet solution. The blue coloration attributed to the solution by Heller is due to the presence of monoanil.

Isatin- α -benzylloxime, $C_6H_4 \langle \begin{smallmatrix} CO \\ NH \end{smallmatrix} \rangle C:N \cdot O \cdot CH_2Ph$, yellow crystals, m. p. 128° (prepared from isatin lactim ether and α -benzylhydroxylamine), yields blue alkali *salts*, differing in this respect from the dianil.

H. W.

Preparation of β -Thionaphthisatin. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 186859).— β -Thionaphthisatin is obtained by the interaction of oxalyl chloride and β -thionaphthol in presence or absence of a diluent or a condensing agent. It forms a red, crystalline powder, m. p. 153°, and is a valuable dye-intermediate. As an example of the preparation, 160 parts of β -thionaphthol may be mixed with 635 parts of oxalyl chloride, and after stirring some hours at the ordinary temperature the mixture is heated to the boiling point. The excess of oxalyl chloride is distilled off, and the β -thionaphthisatin extracted from the residue with aqueous sodium carbonate and reprecipitated from the extract with hydrochloric acid. Some of the oxalyl chloride may, if desired, be replaced by carbon disulphide, and aluminium chloride or sulphuric acid may be added as the condensing agent. G. F. M.

Manufacture of Amino-alcohols of the Quinoline Series. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 185913).—Amino-alcohols derived from 2-phenylquinoline-4-carboxylic acid are obtained by converting the acid, its ester, or nitrile into a 2-phenyl-4-quinolyl alkyl ketone and either reducing the latter through its oximino-compound to the 2-phenylquinolyl-4-amino-alcohol, or causing the ketone, halogenised in the alkyl group, to react with an amine or substituted amine and reducing the 2-phenyl-4-quinolyl aminoalkyl ketone thus produced to the corresponding amino-alcohol. The reactions are represented by the following scheme:



s s* 2

Ethyl 2-phenylquinoline-4-formylacetate, $C_6NH_5Ph \cdot CO \cdot CH_2 \cdot CO_2Et$, prepared by condensing ethyl acetate with ethyl 2-phenylquinoline-4-carboxylate, forms yellow prisms, m. p. 52–54°. By ketonic hydrolysis it is converted into 2-phenyl-4-quinolyl methyl ketone, $C_6NH_5Ph \cdot COMe$, yellow crystals, m. p. 75°. Its hydrobromide forms yellow crystals, m. p. 240°. Its oximino-compound is obtained as sodium salt by the action of amyl nitrite and sodium ethoxide in benzene solution. Liberated by the addition of acetic acid, it forms yellow crystals, m. p. 182° (decomp.). 2-Phenyl-4-quinolyl methyl ketone can be prepared alternatively from 4-cyano-2-phenylquinoline by means of the Grignard reagent as indicated in scheme II above. 2-Phenyl-4-quinolyl bromomethyl ketone is obtained by brominating the ketone in concentrated hydrobromic acid or in organic solvents. The free base forms bright yellow crystals, m. p. 91°. Its hydrobromide also forms intensely yellow crystals, m. p. about 225°. On treatment of the bromoalkyl ketones (1 mol.) with 3 mols. of an amine the corresponding aminoalkyl ketones are formed. As these substances are not very stable, they are best isolated as their hydrochlorides. The preparation of the following is described: 2-phenyl-4-quinolyl dimethylaminomethyl ketone, of which the monohydrochloride is a bright yellow, crystalline powder, m. p. 208° (decomp.); 2-phenyl-4-quinolyl diethylaminomethyl ketone, forming a monohydrobromide in bright yellow, felted needles, m. p. 164° (decomp.); and 2-phenyl-4-quinolyl piperidinomethyl ketone, giving a monohydrochloride, m. p. 235°; and a monohydrobromide, m. p. 241° (decomp. in each case). From the above ketones by hydrogenation in presence of platinum black, or from the oximino-ketone by reduction with zinc dust and formic acid, the corresponding amino-alcohols are obtained (schemes III and IV). The free bases are precipitated from aqueous solutions of their salts in amorphous form. They soon become brown on exposure to air, but form stable mono-acid salts sparingly soluble in water, and diacid salts freely soluble in water. 2-Phenyl-4-quinolylaminoethanol dihydrochloride, $C_6NH_5Ph \cdot CH(OH) \cdot CH_2 \cdot NH_2 \cdot 2HCl$, forms yellow crystals, m. p. 145°. 2-Phenyl-4-quinolyl dimethylaminoethanol dihydrochloride is a pale yellow powder, m. p. 175° (decomp.). The corresponding diethyl compound gives a dihydrochloride, m. p. 180°, and the piperidino-compound a similar salt, m. p. 199°. G. F. M.

Aldehyde Compounds of Hydroxy-amines and the Partial Acylation of these Amines. MAX BERGMANN, REINHOLD UELTS, and FRANCISCO CAMACHO (*Ber.*, 1922, 55, [B], 2796–2812).—Many examples are given of the use of the aldehydic compounds of hydroxy-bases, particularly with respect to the purification of hydroxy-amines and their partial acylation.

p-Aminophenyl benzoate, m. p. 148°, is prepared by a slight modification of the method of Reddelien and Danilof (this vol.,

i, 148). 2:4:5-Triphenyloxazolidine, $\begin{array}{c} CHPh-O \\ | \\ CHPh-NH \end{array} > CHPh$, is converted by benzoyl chloride in the presence of pyridine and subse-

quent treatment of the product with hydrochloric acid into the *N*-benzoate of 'isodiphenylhydroxyethylamine, m. p. 223° (cf. Auwers and Sonnenstuhl, A., 1904, i, 1054).

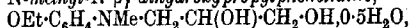
Almost exclusive acylation of the amino-group of hydroxy-bases can be effected by means of acyl polysulphides of the type $R\cdot CO\cdot S_x\cdot COR$. These compounds react rapidly with basic amino-groups, with the formation of acid amides and hydrogen sulphide (sulphur is also liberated from the polysulphides), whereas the alcoholic and phenolic hydroxy-groups are not normally affected. Thus *L*-tyrosine ethyl ester is transformed by benzoyl disulphide in boiling alcoholic solution into the *N*-benzoyl ester, m. p. 120–121° (corr.), from which the corresponding *N*-*L*-benzoyl acid, m. p. 164°, identical with that prepared by Fischer by resolution of synthetic *r*-benzoyl-tyrosine, is obtained. Similarly, *o*-aminophenol and *p*-aminophenol are transformed into *o*-benzoylaminophenol, m. p. 169–171°, and *p*-benzoylaminophenol in excellent yield.

The removal of an acyl group from the nitrogen atom of fully acylated hydroxy-amino-compounds can frequently be effected by the use of phosphorus pentachloride and alcohol (cf. Bergmann, Brand, and Dreyer, A., 1921, i, 444). As an example of the applicability of the method, *o*-aminophenol is transformed into its dibenzoyl derivative, m. p. 179°, which is treated with phosphorus pentachloride at 100°; after distillation of phosphoryl chloride, the residue is treated with ethyl alcohol at 0°, whereby *o*-aminophenyl benzoate hydrochloride, slender needles, m. p. 149° (decomp.), is obtained in 89% yield. The salt is not so unstable as has been assumed previously. When heated above its melting point, warmed with water, or treated with cold sodium acetate solution, it is, however, transformed into *o*-hydroxybenzanilide, which undergoes partial conversion into 2-phenylbenzoxazole, $C_6H_4\langle\overset{O}{\underset{N}{\parallel}}\rangle CPh$, m. p. 163°. The presence of the unsubstituted amino-group in the salt is demonstrated by its diazotisation and subsequent coupling with dimethylaniline to the dye, $NMe_2\cdot C_6H_4\cdot N\cdot N\cdot C_6H_4\cdot CO_2Ph$, red plates, m. p. 116°.

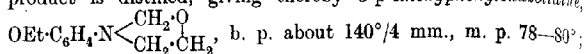
The preparative applicability of aldehydic compounds of hydroxy-bases is illustrated in the case of certain derivatives of phenetidine. The base is converted by glycidate at 0° into a mixture of the secondary and tertiary amines containing one or two dihydroxypropyl residues which can only be separated with difficulty by fractional crystallisation. The mixture is treated with freshly distilled formaldehyde solution at the atmospheric temperature, whereby the secondary base is transformed into 3-*p*-ethoxyphenyl-5-hydroxymethyl-oxazolidine, $OEt\cdot C_6H_4\cdot N\langle\overset{O}{\underset{CH_2}{\parallel}}\rangle CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, b. p. 135–145°/0.3–0.4 mm., m. p. 57–59°, which is readily separated from the tertiary

base by fractional distillation. The oxazolidine derivative is readily decomposed by oxalic acid in alcoholic solution into β-dihydroxypropylphenetidine oxalate, m. p. 161–163°, from which the free base, $OEt\cdot C_6H_4\cdot NH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, m. p. 90–92°, is isolated. The further action of formaldehyde on the oxazolidine

derivative in the presence of hydrochloric acid leads to the production of *N*-methyl-*N*- β -*γ*-dihydroxypropylphenetidine,



m. p. 51—53°, the identity of which is established by its formation from *N*-methylphenetidine and glycidol. In a similar manner, the mixture of bases obtained from *p*-phenetidine, ethylene chlorohydrin, and sodium iodide is treated with formaldehyde and the product is distilled, giving thereby 3-*p*-ethoxyphenyloxazolidine,



the latter is transformed by dilute acids into β -hydroxyethylphenetidine, colourless leaflets, m. p. 50—51° (hydrogen oxalate, m. p. 139—140°). The base is transformed by the further action of formaldehyde in the presence of hydrochloric acid into *N*-methyl- β -hydroxyethylphenetidine, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, b. p. 130°/0.5 mm., m. p. 33—39°. The benzoic ester of the latter, microscopic prisms or hexagonal plates, m. p. 78°, is obtained by means of benzoyl chloride in the presence of pyridine.

β -Hydroxyethylphenetidine is transformed by benzaldehyde into 2-phenyl-3-*p*-ethoxyphenyloxazolidine, $\text{CH}_2 \cdot \text{N} \begin{array}{c} \text{CH}_2 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CHPh} \end{array}$, slender, colourless needles, m. p. 72—73°.

In place of formaldehyde, which gives products of exceptionally low boiling point, other aldehydes or ketones may be employed, thus allowing a modification of the physical properties of the derivatives and also of their mode of production and decomposition.

H. W.

Diethylrhodanine. CLIFFORD SHATTUCK LEONARD (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, 4, No. 14, 1—13).—With the object of studying the effect of ring sulphur in a substance which might be expected to have narcotic properties, diethylrhodanine, $\text{CO} \cdot \text{CEt}_2$, $\text{NH} \cdot \text{CS} \rangle \text{S}$, was prepared, by condensing α -bromo- α -ethylbutyric acid with ammonium dithiocarbamate. It crystallises in needles, m. p. 107.5°. When injected into a rabbit, intramuscularly when dissolved in oil or intravenously when dissolved in sodium hydrogen carbonate solution, it had a narcotic effect slightly greater than that of veronal but with a quicker recovery. Given by the mouth, it was inactive. On account of its low solubility in water (1 in 3000 at 18°), it can have no practical therapeutic value. The bearing of the substance on the theory of narcosis is indecisive. E. H. R.

Selenium Organic Compounds. I. Synthesis of 4-Seleno-2-methylquinazolone, 2-Phenylbenzoselenazole, and some Derivatives of the Latter. MARSTON TAYLOR BOBERT and YÜ-GWAN CHEN (*J. Amer. Chem. Soc.*, 1922, 44, 2352—2357).—*o*-Aminobenzoselenamide, m. p. 116° (corr.), was obtained in very poor yield by saturating a solution of anthranilonitrile in absolute alcohol at 0° with dry hydrogen selenide and dry ammonia and heating the product in a sealed tube at 105—110° for ten hours.

4-*Seleno-2-methylquinazalone*, m. p. 213.5° (corr.), was synthesised from anthranilonitrile by several methods, and found to be rather unstable. On exposure to light and air, it slowly decomposed with separation of finely divided metallic selenium and formation of 2-methyl-4-quinazalone.

2-Phenylbenzoselenazole (cf. Fromm and Martin, A., 1913, i, 1323) was best prepared by gently boiling benzylideneaniline for three days on a sand-bath with selenium dust. On nitration in sulphuric acid solution at below 0°, it gave 6-nitro-2-phenylbenzoselenazole, m. p. 202.4° (corr.). On reduction with tin and hydrochloric acid, this yielded 6-amino-2-phenylbenzoselenazole, m. p. 201.2—202.3° (corr.), giving an acetyl derivative, m. p. 188.1—188.7° (corr.), and a benzylidene derivative, m. p. 156.7—157.6° (corr.). The amine, when diazotised and the product coupled with β -naphthol, gave 2-phenylbenzoselenazole-azo- β -naphthol, m. p. 284.2° (corr.), which dyed silk a fine pink. The diazotised amine was similarly coupled with a number of phenols and amines, and most of the azo-compounds dyed silk. If the nitration of the phenylbenzoselenazole was pushed further (?) 4:6-dinitro-2-phenylbenzoselenazole, m. p. 246.8° (corr.), was obtained and on reduction gave (?) 4:6-diamino-2-phenylbenzoselenazole, m. p. 269—270.5°, which yielded a diacetyl derivative, m. p. 239.5—240.5°, and a dibenzylidene derivative, m. p. 186—187°. The diamine was diazotised and coupled with a number of phenols and amines, giving new selenium azo-dyes.

W. G.

3-Chloro-1-alkylpyrazoles and 1-Alkylpyrazol-3-one.

C. A. ROJAHN (*Ber.*, 1922, **55**, [B], 2959—2971).—1-Alkyl derivatives of 3-chloropyrazole are formed by the alkylation of chloromethylpyrazole under certain conditions. In each case, two isomerides are obtained by the alkylation of 3-methyl- or 3-phenyl-pyrazolones, among which 1:5-dimethylpyrazol-3-one has been almost certainly identified.

5-Chloro-3-methylpyrazole dissolved in anhydrous ether is converted by sodium into its soluble sodium salt, which is transformed by a slight excess of methyl iodide at 100° into 3-chloro-1:5-dimethylpyrazole, $\text{NMe} \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{N} = \text{CCl} \end{smallmatrix}$, plate-like crystals, m. p. 45—

47°, b. p. 208—210° (slight decomp.)/atmospheric pressure, 138°/72 mm. The substance may also be prepared by the action of methyl toluene-*p*-sulphonate on the sodium compound; in this case, 5-chloro-1:3-dimethylpyrazole, b. p. 155—160°, is also produced. The course of the reaction is somewhat unusual, and is most readily explained by an initial addition of methyl iodide and subsequent elimination of sodium iodide in accordance with the scheme:

$$\begin{array}{c} \text{N} \begin{smallmatrix} \text{NNa} \cdot \text{CCl} \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} \rightarrow \text{I} \begin{smallmatrix} \text{CH}_3 \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{N} = \text{CCl} \end{smallmatrix} \rightarrow \text{MeN} \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{N} = \text{CCl} \end{smallmatrix} \end{array}$$

The validity of the constitution assigned to the product depends on a comparison of its properties with those of previously described chlorodimethylpyrazoles and the demonstration that it contains an unsubstituted CH group in position 4 and a methyl group

attached to the nitrogen atom in position 1 as evidenced by its insolubility in alkali hydroxide and its conversion into 3-chloro-4-nitroso-1:5-dimethylpyrazole, green needles, m. p. 87°, and 3-chloro-4-bromo-1:5-dimethylpyrazole, long needles, m. p. 56°. 3-Chloro-1:5-dimethylpyrazole 2-methiodide, colourless, crystalline leaflets, decomp. 184°, is prepared by the successive action of methyl sulphate and potassium iodide on the parent pyrazole. 3-Chloro-5-methyl-1-ethylpyrazole, an almost colourless liquid, b. p. 216–218°/atmospheric pressure, is obtained by the action of ethyl iodide on the sodium derivative of 5-chloro-3-methylpyrazole; it is converted by bromine in the presence of glacial acetic acid into 3-chloro-4-bromo-5-methyl-1-ethylpyrazole, m. p. 39°. 3-Chloro-5-methyl-1-benzylpyrazole, b. p. 295–300°, is obtained in a similar manner.

5-Chloro-3-phenylpyrazole is converted by successive treatment with sodium and methyl alcohol and methyl toluene-*p*-sulphonate into chlorophenylmethylpyrazole, m. p. 43°, b. p. 295–297°/atmospheric pressure, which with bromine in glacial acetic acid solution gives 1-chloro-4-bromo-3-phenyl-1-methylpyrazole, needles, m. p. 67°.

5-Chloro-3:4-dimethylpyrazole is prepared by the action of phosphoryl chloride on 3:4-dimethylpyrazol-5-one, m. p. 266°; it crystallises in long needles, m. p. 124–125°, b. p. 251–252°/atmospheric pressure. It does not give a bromo-derivative, 5-chloro-1-benzoyl-3:4-dimethylpyrazole forms long, silky needles, m. p. 90–91°.

3-Chloro-1:5-dimethylpyrazole is transformed by ethyl bromide at 180–200° owing to interchange of alkyl groups into 3-chloro-5-methyl-1-ethylpyrazole ethobromide, coarse crystals, m. p. 225° (decomp.), which is converted by heat into 3-chloro-5-methyl-1-ethylpyrazole, b. p. 215–220°.

3-Methylpyrazol-5-one is converted by methyl iodide and methyl alcoholic sodium methoxide solution at 100° into a mixture of 1-methylantipyrine, b. p. 310°/760 mm., and 1:5-dimethylpyrazol-3-one, $\text{NMe} \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \diagup \\ \text{N} = \text{C} \cdot \text{OH} \end{smallmatrix}$ or $\text{NMe} \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \diagdown \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$, m. p. 172–173°.

Under similar conditions, the latter compound is generally obtained when methyl toluene-*p*-sulphonate is used as methylating agent, but on one occasion a previously undescribed dimethylpyrazolone, m. p. 181–182° (bromide, m. p. 218°), was formed; the preparation of this compound could not be repeated. 4-Bromo-1:5-dimethylpyrazol-3-one crystallises in small, colourless needles, m. p. 209°.

5-Methyl-1-ethylpyrazol-3-one, colourless needles, m. p. 135–136° (bromo-derivative, m. p. 39°), is prepared from 3-methylpyrazol-5-one, ethyl iodide and ethyl alcoholic sodium ethoxide solution.

The alkylation of 3-phenylpyrazol-5-one with methyl toluene-*p*-sulphonate leads to the formation of two phenyl-1-methylpyrazolones, m. p. 165° and 96°, respectively: the former is converted by phosphoryl chloride at 210° into 5-chloro-3-phenyl-1-methylpyrazole, m. p. 62–63°, whereas under similar conditions the latter is resinsified.

1:5-Dimethylpyrazole, m. p. 173°, is transformed by phosphoryl

chloride at 200—210° into 3-chloro-1:5-dimethylpyrazole, m. p. 46—47°.
H. W.

Molecular Compounds of Diketopiperazine and Phenols. G. PGVARNIN and P. TICHOMIROV (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 40—46).—When 10—15% aqueous solutions of diketopiperazine (1 mol.) and a phenol (1 mol.), either with or without a few drops of 10% sulphuric acid solution, are boiled together for some minutes, crystalline molecular compounds of the two components are formed. These are decomposed by solvents of the phenols with the exception of water, and when heated lose phenol and do not melt, but sometimes carbonise.

Diccatechol-diketopiperazine and *diresorcinol-diketopiperazine*, $2C_6H_6O_2 \cdot C_4H_6O_2N_2$, form colourless crystals. *Monoquinol-diketopiperazine*, $C_6H_6O_2 \cdot C_4H_6O_2N_2$, forms a stable lilac form and a labile white form. *Dipyrogallol-diketopiperazine*, $2C_6H_6O_3 \cdot C_4H_6O_2N_2$, and *protocatechuic acid-di-diketopiperazine*, $C_7H_6O_4 \cdot 2C_4H_6O_2N_2$, form white crystals. Diketopiperazine yields condensation products with protocatechualdehyde and furfuraldehyde, and an unstable compound with phenol.

The theory of oscillating affinity is applied in arriving at an explanation of the structure of these compounds. T. H. P.

Bromo-derivatives of 2-Methylglyoxaline. LOUIS LIGHT and FRANK LEE PYMAN (*T.*, 1922, 121, 2626—2630).

Orientation of the 1:4- and 1:5-Dimethylglyoxalines.
Mode of Fission of 5-Aminoglyoxalines. FRANK LEE PYMAN (*T.*, 1922, 121, 2616—2626).

The Reactions of the Formamidines. X. The Thioimidazolones [Thiolglyoxalones]. F. B. DAINS, RUTH THOMPSON, and W. F. ASENDORF (*J. Amer. Chem. Soc.*, 1922, 44, 2310—2315).—2-Thio-4-glyoxalone and its mono- and di-substituted derivatives react readily with formamidines, giving 5-R-aminomethylene derivatives. The following compounds are described: 2-thiol-1:3-diphenyl-5-anilinomethylene-4-glyoxalone, m. p. 175°; 2-thiol-1-phenyl-3-p-tolyl-5-anilinomethylene-4-glyoxalone, m. p. 197—198°; 2-thiol-3-phenyl-5-anilinomethylene-4-glyoxalone, m. p. 252°; 2-thiol-3-p-tolyl-5-anilinomethylene-4-glyoxalone, m. p. 250°; 2-thiol-3-o-tolyl-5-anilinomethylene-4-glyoxalone, m. p. 215°; 2-thiol-3-m-tolyl-5-anilinomethylene-4-glyoxalone, m. p. 207—208°; 2-thiol-3-p-chlorophenyl-5-anilinomethylene-4-glyoxalone, m. p. 274—276°; 2-thiol-3-p-ethoxyphenyl-5-anilinomethylene-4-glyoxalone, m. p. 227°; 2-thiol-3-phenyl-5-p-bromophenylaminomethylene-4-glyoxalone, m. p. 190°; 2-thiol-3-phenyl-5-naphthylaminomethylene-4-glyoxalone, m. p. 160°.

Two new thioimidazolones were prepared, namely, 2-thiol-3-m-tolyl-4-glyoxalone, m. p. 167°, and 2-thiol-3-p-chlorophenyl-4-glyoxalone, m. p. 234·5°.

The above anilinomethyleneglyoxalones react with alkyl haloids to give alkyl-thio-ethers, of which there were prepared: 2-methylthiol-3-phenyl-5-anilinomethylene-4-glyoxalone, m. p. 173°;

2-ethylthiol-3-phenyl-5-anilinomethylene-4-glyoxalone, m. p. 164.5°;
 2-n-butylthiol-3-phenyl-5-anilinomethylene-4-glyoxalone, m. p. 124°;
 2-allylthiol-3-phenyl-5-anilinomethylene-4-glyoxalone, m. p. 218°;
 2-benzylthiol-3-phenyl-5-anilinomethylene-4-glyoxalone, m. p. 145°;
 2-benzylthiol-3-o-tolyl-5-anilinomethylene-4-glyoxalone, m. p. 148°;
 2-benzylthiol-3-m-tolyl-5-anilinomethylene-4-glyoxalone, m. p. 154°;
 2-benzylthiol-3-p-ethoxyphenyl-5-anilinomethylene-4-glyoxalone, m. p. 170°.

When hippuric acid and phenylthiocarbimide were heated together at 150° for one and a half hours 2-thiol-1-benzoyl-3-phenyl-4-glyoxalone, m. p. 177—179°, was obtained, and yielded 2-thiol-1-benzoyl-3-phenyl-5-anilinomethylene-4-glyoxalone, m. p. 184—186°. Similar compounds are 2-thiol-1-benzoyl-3-m-tolyl-4-glyoxalone, m. p. 197°; 2-thiol-1-benzoyl-3-m-tolyl-5-anilinomethylene-4-glyoxalone, m. p. 187°; 2-thiol-1-benzoyl-3-p-ethoxyphenyl-4-glyoxalone, m. p. 168°; 2-thiol-1-benzoyl-5-anilinomethylene-4-glyoxalone, m. p. 164—165° and its 2-benzylthio-ether, m. p. 165°; and 2-thiol-5-anilinomethylene-4-glyoxalone, m. p. 264°.

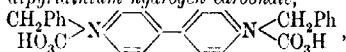
When boiled for six hours with a mixture of alcohol and hydrochloric acid, 2-thiol-1-benzoyl-3-phenyl-4-glyoxalone was hydrolysed, giving aniline, a little benzoic acid, and hippuric acid. The 5-anilinomethylene derivative behaved similarly.

W. G.

The Synthesis of *m-z*-Benzispyrrole Derivatives.

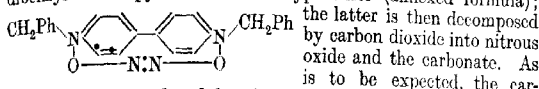
WILLIAM DAVIES and EDGAR HERBERT CUTHBERT HICKOX (T., 1922, 121, 2640—2653).

Free Ammonium Radicles. IV. Further Investigations on 1:1'-Dibenzyl-4:4'-dipyridinium and its Homologues and on the so-called 1:1'-Disubstituted Tetrahydro-4:4'-dipyridyls. ERNST WEITZ and THEODOR KÖNIG (Ber., 1922, 55, [B], 2864—2889).—It has been observed recently by Weitz and Ludwig (this vol., i, 365) that the dark blue solution of 1:1'-dibenzyl-4:4'-dipyridinium, $\text{CH}_2\text{Ph}\cdot\text{N}^+\text{C}_5\text{H}_4\cdot\text{C}_5\text{H}_4\cdot\text{N}^+\cdot\text{CH}_2\text{Ph}$, in methyl alcohol reacts with nitric oxide, but a definite product of the change could not be isolated. A repetition of the action in chloroform solution has led to the surprising isolation of 1:1'-dibenzyl-4:4'-dipyridinium hydrogen carbonate,



a colourless substance which decomposes rapidly on exposure to air, but is more stable in an atmosphere of carbon dioxide. It decomposes with evolution of gas at about 80° after blackening at about 65°. It dissolves readily in water to an alkaline solution and is converted by potassium iodide and perchloric acid into dibenzylidipyridinium iodide, m. p. 248—249°, and dibenzylidipyridinium perchlorate, m. p. 257°, respectively. Carbon dioxide is by itself without action on the radicle; the nitric oxide acts as an oxidising agent, being reduced to nitrous oxide the formation of which is established experimentally. In all probability an unstable nitroso-derivative, $\begin{array}{c} \text{CH}_2\text{Ph} \\ | \\ \text{ON} > \text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_5\text{H}_4 \quad \text{C}_5\text{H}_4 \\ \diagdown \quad \diagup \end{array} \text{N} < \begin{array}{c} \text{CH}_2\text{Ph} \\ | \\ \text{NO} \end{array} \end{array}$

is primarily formed which passes into the isomeric salt, 1:1'-dibenzyl-4:4'-dipyridinium-1:1'-hyponitrite (annexed formula);



the latter is then decomposed by carbon dioxide into nitrous oxide and the carbonate. As is to be expected, the carbonate is also produced by the combined action of oxygen and carbon dioxide on 1:1'-dibenzyl-4:4'-dipyridinium, whereby approximately one atom of oxygen is absorbed by each molecule of the radicle. The action of oxygen or air alone leads to the formation of only very small amounts of soluble and alkaline products, as is to be expected when the instability of the anhydride is taken into consideration.

In a similar manner, the so-called 1:1'-dibenzyltetrahydro-4:4'-dipyridyl of Hofmann and Emmert (bis-*N*-benzylpyridinium according to the author) is converted by carbon dioxide and oxygen in chloroform solution into unimolecular 1-benzylpyridinium hydrogen carbonate, $\text{C}_5\text{H}_5\text{N}(\text{C}_6\text{H}_5)\cdot\text{CO}_2\text{H}$; dibenzyl-4:4'-dipyridinium hydrogen carbonate is formed simultaneously in subordinate amount. A similar result is obtained when nitric oxide is substituted for oxygen.

The reduction of 1:1'-dibenzyl-4:4'-dipyridinium salts (chloride and iodide) to the radicle by metals in different media in the absence of acids has been investigated. The blue solutions in acetone are characterised by relative stability towards air (although they react instantaneously with iodine). Similar solutions prepared electrolytically or from the crystalline radicle behave in an analogous manner. On the other hand, the solutions of the dihaloids in acetone are reduced when heated with copper gauze, whereas the similar solutions in water or methyl alcohol are only affected by less noble metals such as zinc. In explanation of these observations, the hypothesis is put forward that the radicle exists in a readily oxidisable form, the corresponding salts of which resemble ammonium salts, and a difficultly oxidisable condition which gives rise to quinone-like haloids. The two extremes may be represented by the scheme $\text{R}\cdot\text{N} \text{---} \text{C}_5\text{H}_4 \text{---} \text{C}_5\text{H}_4 \text{---} \text{N}\cdot\text{R} \rightleftharpoons \text{R}\cdot\text{N} \text{---} \text{C}_5\text{H}_4 \text{---} \text{C}_5\text{H}_4 \text{---} \text{N}\cdot\text{R}$, but the authors regard the two forms, on account of the subsidiary valencies, as rather less distinct from one another than is thus suggested.

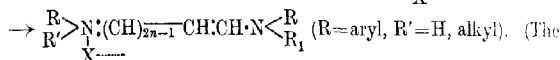
If the correctness of the formula $\text{RN} \text{---} \text{C}_5\text{H}_4 \text{---} \text{C}_5\text{H}_4 \text{---} \text{NR}$ is regarded as established, 2- or 3-alkylpyridines would be expected to yield radicles; in the case of 4-alkylpyridines, this is impossible unless the alkyl group suffers replacement. It is found that the almost colourless, oily product of the reduction of 2-methylpyridinium benzyl chloride by sodium amalgam gives a blue coloration, due to the corresponding radicle, when its alcoholic solution is heated; it is readily oxidised. Similarly, 2:6-dimethylpyridine is converted by benzyl iodide into the corresponding benzyl iodide, which is reduced to two products, one of which has m. p. 121° , whereas the

other remains semi-solid; either substance gives a blue radicle coloration when its alcoholic solution is warmed in contact with air. On the other hand, *bis*-1-benzyl-2:4-dimethylpyridinium, obtained as a pale yellow, viscous liquid by reduction of 2:4-dimethylpyridinium benzyl chloride, does not develop a blue coloration when its alcoholic solution is heated. A similar behaviour is observed with *bis*-1-benzyl-2:4:6-trimethylpyridinium, colourless needles, m. p. 102–103°, which is prepared by the reduction of 2:4:6-trimethylpyridinium benzyl iodide, pale yellow crystals, m. p. 102° (corresponding perchlorate, m. p. 135°). The action of iodine on the new "leuco-compounds" dissolved in cold chloroform leads invariably to the formation of the corresponding mono-iodides; if the titration is performed rapidly, the derivatives substituted in position 4 absorb almost exactly one molecular proportion of iodine, thus giving two molecular proportions of the mono-iodide thus: $C_5NH_2Me_3(C_6H_5)_2 + I_2 \rightarrow 2C_5NH_2Me_3(C_6H_5)I$; the reaction with the 2-methyl derivative is less quantitative. *Bis*-1-benzyl-2:4:6-trimethylpyridinium is rapidly decomposed by carbon dioxide and nitric oxide when dissolved in chloroform, but an alkaline hydrogen carbonate or a derivative soluble in water could not be isolated. *Bis*-1-benzyl-2:4:6-trimethylpyridinium is decomposed rapidly in boiling benzene into 2:4:6-trimethylpyridine and dibenzyl: $2C_5NH_2Me_3\cdot CH_2Ph \rightarrow 2C_5NH_2Me_3 + (CH_2Ph)_2$. The rapid decomposition of the molecule is obvious during determinations of the molecular weight in boiling benzene, whereas the bimolecular compound is completely stable in the freezing solvent. New determinations of the molecular weight of bisbenzylpyridinium in freezing benzene have given accurately bimolecular values, whereas in the boiling solvent the molecular weight diminishes gradually but much more slowly than that of the collidyl compound. *Bis*-1-methyl-2:4:6-trimethylpyridinium appears to be practically stable in boiling benzene.

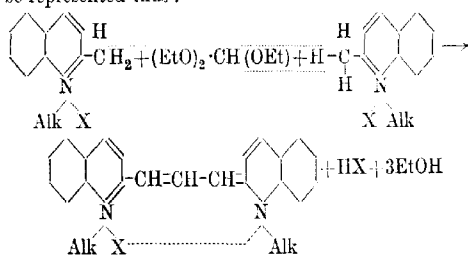
If an alcoholic solution of 1:1-dibenzyl-4:4'-dipyridinium dichloride or di-iodide is treated with solid or dissolved bisbenzylpyridinium, the intensely oxidisable blue coloration of the radicle is immediately developed. The same effect is produced by other leuco-compounds. Similarly, the action of bisbenzylpyridinium on 1:1-diphenyl-4:4'-dipyridinium di-iodide causes the production of the intensely emerald green diphenyl radicle. The action appears to be most readily explained by the hypothesis that the leuco-compounds—as in their action towards iodine, etc.—behave as unimolecular radicles, passing into the corresponding iodides and liberating the nobler dipyridinium radicle: $I(R)N:C_5H_4\cdot C_5H_4\cdot N(R)\cdot I + 2C_5H_5\dot{N}(R) \rightarrow R\dot{N}:C_5H_4\cdot C_5H_4\cdot \dot{N}R + H.W.$

The Constitution of the Pinacyanols, a Contribution to the Chemistry of the Quinocyanines. W. KÖNIG (*Ber.*, 1922, 55, [B], 3293–3313).—Constitutional formulæ for pinacyanol have been proposed by O. Fischer (*A.*, 1921, i, 56), Wise, Adams, and Lund (*A.*, 1919, i, 416), and Mills and Hamer (*T.*, 1920, 117, 1150;

cf. Braunscholtz, T., 1922, **121**, 169). Objection is raised to the first of these, since its carbon atom with twin double bonds places it in a category by itself and quite apart from the other quinocyanines, and to the second since it represents pinacyanol as a peculiar member of the class of lepidinecyanines and does not take into account its oxidation to *N*-alkyl-2-quinolones and the differences between the sensitising effect of the cyanines (in the narrower sense) and the pinacyanols and in their behaviour towards acids. The conception of Mills and Hamer is thus considerably strengthened. It is deduced, however, mainly from the results of oxidative degradation of the pinacyanols. Confirmatory evidence in its favour is brought by two different methods. A comparison of the absorption spectra of pinacyanol and ψ -isocyanine and estimation of their persistence and maxima shows that the same differences exist between them as between polymethine dyes and the compounds obtained from them by the streptostatic introduction of a vinylene group into the chromophore system, thus:
$$\begin{array}{c} \text{R} > \text{N}^+ \text{---} (\text{CH})_{2n-1} \text{N}^+ < \text{R} \\ | & | \\ \text{X} & \text{X} \end{array}$$



description of this work will be published elsewhere.) The second confirmation of Mills and Hamer's formula is obtained by a direct synthesis of pinacyanol. For this purpose, quinaldinium salts are condensed with ethyl orthoformate in the presence of suitable agents such as acetic anhydride or zinc chloride, whereby pinacyanols are readily prepared in about 50% yield. The synthesis may be represented thus:



It is thus similar to the author's syntheses of pentamethine dyes of the indole series. Since it is also found that 4-methylquinolinium salts can condense, although with greater difficulty, with orthoformic ester, it is expected that the dicyanines will also prove capable of synthesis along these lines. The ability of the quinoline derivative to enter into the reaction is considered to be due to the formation from it of the methylene base in accordance with the scheme
$$\begin{array}{c} \text{C}_6\text{H}_4 < \text{CH} \text{---} \text{CH} \\ | & | \\ \text{N}^+ \text{---} \text{CMe} & \rightleftharpoons \text{C}_6\text{H}_4 < \text{CH} \text{---} \text{CH} \\ & | \\ & \text{N}^+ \text{---} \text{C} \text{---} \text{CH}_2 \\ & | \\ & \text{Alk} \text{---} \text{X} \end{array} + \text{HX}.$$

possible mechanism of the synthesis is discussed at length, but the original communication should be consulted for details.

Since the constitution of the cyanines has been largely elucidated, the author considers it desirable that the common names (cyanines, isocyanines, ψ -isocyanines, dicyanines, ψ -dicyanines, carbocyanines, and cryptocyanines) should be deleted from the scientific literature and replaced by the general term quinocyanines, by which is understood the salts of quinolyldihydroquinolylenemethanes which are not methylated at the nitrogen atom. The three classes, 2:2', 2:4', and 4:4'-quinocyanine salts are thus suitably distinguished. The further derivatives are termed benzothiazocyanines (thiocyanines) and indoleninocyanines (indocyanines). Further types are produced by the streptostatic introduction of n -vinylene-groups between the quinoline residues and are designated mono- (di-, tri-, etc.) vinylene-2:2'- or 2:4'- or 4:4'-quinocyanine salts. As examples may be quoted: dimethyl- ψ -isocyanine iodide = 1:1'-dimethyl-2:2'-quinocyanine iodide; pinaverdol = 1:6:1'-trimethyl-2:4'-quinocyanine iodide; ψ -dicyanine bromide = 1:1'-diethyl-4:6:4':6'-tetramethylstreptomonoxyvinylene-2:2'-quinocyanine bromide; dicyanine = 1:1'-diethyl-4:6:2':6'-tetramethylstreptomonoxyvinylene-2:4'-quinocyanine iodide.

[With H. ZORN.]— ψ -isocyanine iodide [1:1'-dimethyl-2:2'-quinocyanine iodide] is synthesised by heating 2-chloroquinoline with quinaldine methiodide at 211° and treating the product successively with methyl sulphate and potassium iodide.

Pinacyanol iodide [1:1'-diethylstreptomonoxyvinylene-2:2'-quinocyanine iodide] is prepared by the gradual addition of ethyl orthoformate to a solution of quinaldine ethiodide in gently boiling acetic anhydride. 1:1'-Dimethylstreptomonoxyvinylene-2:2'-quinocyanine iodide is obtained in a similar manner. The synthesis is capable of wide variation. The ester may be added to a solution of the quinaldinium salts in boiling nitrobenzene or the quaternary salts may be dissolved in quinaldine or pyridine and heated for some time under a reflux condenser with zinc chloride and the ortho-ester. Trihalogenomethanes, in particular iodoform, may be used in these syntheses. H. W.

Di- and Tri-quinolylmethanes united by the Pyridine Nuclei. III. Symmetrical Di-2-quinolyl Ketone. GÜNTER SCHEIBE and GUSTAV SCHMIDT (*Ber.*, 1922, 55, [B], 3157—3160; cf. A., 1921, i, 62, 451).—Di-2-quinolyl ketone, colourless prisms, m. p. 164°, is obtained by the atmospheric oxidation of di-2-quinolylmethane dissolved in alcohol or acetic anhydride or by the action of dilute nitric acid on di-2-quinolylmethane. It is most conveniently prepared by condensing the latter with p -nitrosodimethylaniline to the compound $(C_9H_6N)_2C:N-C_6H_4-NMe_2$, yellow crystals, m. p. 252°, which is hydrolysed subsequently by dilute acid to the desired ketone and p -aminodimethylaniline. The ketone yields a *picrate*, m. p. 179°, a *phenylhydrazone* (also prepared by coupling di-2-quinolylmethane with benzenediazonium chloride), m. p. 199°, an *oxime* (also derived from di-2-quinolylmethane and

nitrous acid), colourless prisms, m. p. 201°, and an *anil*, m. p. 161°. When warmed with aniline at 120—130° the ketone yields a colourless compound, m. p. 120°, which appears to contain two molecular proportions of aniline.

II. W.

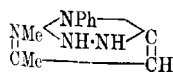
Extension of the Kishner-Wolff Method of Reduction. II.

ERNST THIELEPAPE and OTTO SPRECKEISEN (*Ber.*, 1922, 55, [B], 2929—2939).—The applicability of the method to derivatives of quinoline has been examined previously (this vol., i, 271). It has now been applied successfully to pyridine compounds. In the pyrazole series, on the other hand, difficulties are experienced in the preparation of the hydrazino-compounds on account of displacement reactions and the compound which has been isolated is decomposed in a different direction.

2-Hydrazinopyridine, b. p. 130°/12 mm. (cf. Fargher and Furness, *T.*, 1915, 107, 638) is decomposed when heated with potassium hydroxide at 140—160° with formation of pyridine, but the change proceeds slowly, and is not complete after fourteen hours; it is much more readily effected by copper sulphate or ferric chloride in boiling aqueous solution. 2:6-Dichloropyridine-4-carboxylic acid is converted by the successive action of hydrazine hydrate at the temperature of boiling water and copper sulphate into 2-chloropyridine-4-carboxylic acid, m. p. 245° (decomp.), and by boiling hydrazine hydrate and copper sulphate into isonicotinic acid, m. p. 304° (in sealed tube).

1-Phenyl-3-methylpyrazol-5-one is converted by boiling hydrazine hydrate into phenylhydrazine and 3-methylpyrazol-5-one. The latter reacts with hydrazine hydrate at 150—160° to give ammonia and 4:4'-bis-3-methylpyrazol-5-one.

Antipyrine does not appear to react with boiling hydrazine hydrate, by which, however, it is converted at 180° into *s*-phenylmethylhydrazine and 4:4'-bis-3-methylpyrazol-5-one. The reaction appears to be remarkably dependent on the temperature employed. 5-Chloro-1-phenyl-3-methylpyrazole does not appear to react with hydrazine hydrate at 220°, whereas its methochloride [antipyrine chloride] is readily transformed into hydrazinopyrine, a yellow liquid which solidifies to a glassy solid when cooled in liquid air, but re-melts at the atmospheric temperature. It decomposes slowly on exposure to air, very rapidly when distilled. After prolonged exposure to air, it is only incompletely soluble in ether, leaving a residue, m. p. 155—156°. Hydrazinopyrine picrate forms star-shaped crystals, m. p. 126°. Hydrazinopyrine does not decompose in the normal manner when treated with potassium hydroxide, sodium ethoxide, or copper sulphate; it appears doubtful if it contains a free hydrazone group, and the constitution shown



in the annexed formula is suggested for it. The product obtained by means of potassium hydroxide, sodium ethoxide, or boiling water crystallises in colourless or pale yellow prisms, m. p. 130°, is soluble in dilute acids, and neutral towards litmus. It reduces Fehling's solution readily in the cold. It is scarcely affected

by boiling concentrated hydrochloric acid. Analyses and determinations of molecular weight agree with the formula $C_{14}H_{16}N_4$. It gives a *monopicrate*, m. p. 195° (decomp.), and a *di-methiodide*, $C_{16}H_{22}N_4I_2$, colourless crystals, m. p. 188° after previous softening. It is converted quantitatively by boiling dilute nitric acid into a *dinitro-derivative*, $C_7H_6N_2(NO_2)_2$, microscopic, yellow crystals which do not melt below 280° . The substance appears most probably to be 1:4-diphenylhexahydro-1:2:4:5-tetrazine, $NPh<\begin{smallmatrix} CH_2 \cdot NH \\ NH \cdot CH_2 \end{smallmatrix}>NPh$; if this is the case, its stability towards hydrochloric acid is somewhat remarkable, as is also the production of a *monobenzoyl derivative*, colourless crystals, m. p. 90° .

H. W.

Physical Chemistry of Colloidal and Supersaturated Solutions of Uric Acid. H. SCHADE (*Z. Klin. Med.*, 1922, 93, 1—65; from *Chem. Zentr.*, 1922, iii, 622—623; cf. A., 1913, i, 404, 910).—Further observations on colloidal and supersaturated uric acid (urate) solutions. The colloidal solution is a labile system from which uric acid gel and, finally, crystalline uric acid are formed. Optimum stability is found at p_H 6.0 which is the isoelectric point. Stability is also greater at low temperatures. Supersaturated solutions of uric acid develop a colloidal character owing to aggregation in the disperse phase. The presence of a uric acid-urate complex with amphoteric properties is postulated. Increasingly favourable effect of kations on colloidal stability is shown by the series $NH_4 < Na < K < Li$.

G. W. R.

Decomposition of Dithiocarbazinates. SIMA M. LOSANTICH (*T.*, 1922, 121, 2542—2545).

The Capacity for Migration of Acyl Residues in Acyl Derivatives of the Phenylhydrazones of Hydroxy-ketones. K. VON AUWERS, E. HILLIGER, and E. WULF (*Annalen*, 1922, 429, 190—246).—In continuation of previous work on the migration of acyl groups from oxygen to nitrogen in these substances, two groups of experiments are now described, one relating to derivatives of 3-propionyl-*p*-cresol, and the other to derivatives of 7-hydroxy-1-hydrindone.

The main difficulty in the case of 3-propionyl-*p*-cresol is the lability of the *O*-acyl derivatives which usually undergo hydrolysis in the attempt to prepare their phenylhydrazones. Thus the *acetate*, which is prepared with the help of acetyl chloride, and forms short needles, m. p. 58° , gives the *phenylhydrazone* of the free hydroxy-ketone, needles or leaflets, m. p. 146° , when treated with phenylhydrazine. The *benzoate*, prisms, m. p. 97° , prepared by the Schotten-Baumann method, gives an *oxime*, prisms, m. p. 138 — 138.5° ; the *acetate*, on the other hand, gives the *oxime* of the free hydroxy-ketone when treated with hydroxylamine under similar conditions. The *anil* of the hydroxy-ketone is easily obtained, but the aniline residue is eliminated when the attempt is made to acetylate or benzoylate. The *p*-nitrophenylhydrazone

of the hydroxy-ketone, orange-red needles, m. p. 187—188°, is obtained by the action of *p*-nitrophenylhydrazine on either the hydroxy-ketone itself or its acetyl derivative; the benzoyl derivative, however, yields a *p*-nitrophenylhydrazone, m. p. 159—160°, without elimination of the acyl group. The benzoyl derivative also yields a phenylhydrazone, prisms, m. p. 92°, which on energetic reduction gives aniline and 3- α -benzoylaminopropyl-*p*-cresol, small needles, m. p. 145—146°, a migration of a benzyl group having occurred at some stage of the reaction. On heating the same benzoyl compound with acetic acid, α -benzoyl- β -acetyl- α -phenylhydrazine and 2-*p*-hydroxy-*m*-tolyl-3-methylindole, m. p. 176°, are produced. Attempts to convert the phenylhydrazones of the hydroxy-ketone itself, and of acetophenone, and 3-acetyl-*p*-cresol, into indoles met with no success. The benzoylphenylhydrazone of acetophenone forms needles, m. p. 125.5°.

7-Hydroxy-4-methyl-1-hydrindone is converted successively into its *O*-acetate, needles, m. p. 107°, and the phenylhydrazone of the *O*-acetate, m. p. 226°, which on boiling with acetic acid is isomerised into the *N*-acetyl derivative, prisms, m. p. 130—131°. This, on further acetylation, gives the *ON*-diacetyl derivative, needles, m. p. 132.5°. The *O*-benzoate, m. p. 124°, yields a phenylhydrazone, m. p. 247°, which may also be obtained by benzoylating the phenylhydrazone of the hydroxy-ketone. An attempt to convert this into the benzoylphenylhydrazone, m. p. 115—116°, was not successful, but this hydrazone was actually obtained from benzoylphenylhydrazine and the hydroxy-ketone. The *O*-benzoyl-*N*-acetyl derivative of the phenylhydrazone, prepared either by acetylation of the phenylhydrazone of the benzoate or by the action of acetylphenylhydrazine on the benzoate itself, has m. p. 192—192.5°, and on reduction gives acetanilide and the *N*-benzoyl derivative, m. p. 166—168°, of 7-hydroxy-4-methyl-1-hydrindamine. The *N*-benzoyl-*O*-acetyl derivative, m. p. 152.5—153.5°, prepared from benzoylphenylhydrazine and the acetate of the hydroxy-ketone, on reduction gave benzanilide and the *N*-acetyl derivative, m. p. 158°, of the same hydroxymethylhydrindamine.

The *p*-nitrophenylhydrazone of the hydroxy-ketone has m. p. 298°, its *O*-acetate, m. p. 264—265°, and its *O*-benzoate, m. p. 299° (decomp.). The anil of the hydroxy-ketone has m. p. 88—89°, its oxime, m. p. 140°, and the dibenzoyl derivative of the oxime, m. p. 186.5—187.5°. The oxime on reduction gives 7-hydroxy-4-methyl-1-hydrindamine, which is isolated as its dibenzoyl derivative, m. p. 150°. 7-Methoxy-4-methyl-1-hydrindone gives a phenylhydrazone, m. p. 150—152°, a *p*-nitrophenylhydrazone, m. p. 215°, and a phenylmethylhydrazone, m. p. 83—85°.

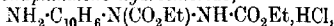
7-Hydroxy-2:4-dimethyl-1-hydrindone gives a phenylhydrazone, m. p. 136.5°, an *O*-acetate, m. p. 91.5—92°, and an *O*-benzoate, m. p. 113°. The phenylhydrazone yields an *O*-acetate, m. p. 184.5—185.5°, and an *O*-benzoate, m. p. 232°, which does not undergo isomeric change similarly to its lower homologue. The *N*-benzoyl derivative of the hydrazone has m. p. 133—135°, and the *N*-acetyl derivative of the *O*-benzoate of the phenylhydrazone has m. p. 171°.

7-Hydroxy-3:4-dimethyl-1-hydrindone gives a *phenylhydrazone*, m. p. 166.5—167.5°, an *O-acetate*, m. p. 135°, and an *O-benzoate*, m. p. 106°; the hydrazone gives an *O-acetate*, m. p. 210—211°, and an *O-benzoate*, m. p. 221—222°, which on heating with acetic acid is converted into the *N-benzoyl* derivative, m. p. 147—148.5°, also prepared from the hydroxy-ketone and benzoylphenylhydrazine. The *O-acetyl-N-benzoyl* derivative of the hydrazone is obtained by acetylation of the *N-benzoyl* derivative, and has m. p. 176.5—177°.

5-Hydroxy-1-hydrindone gives a *benzoyl* derivative, a *phenylhydrazone*, m. p. 165—166°, an *O-benzoyl* derivative of the phenylhydrazone, m. p. 180—181°, and an *N-benzoyl* derivative, m. p. 227°, prepared by using benzoylphenylhydrazine. C. K. I.

The Azo-ester Reaction with Amines and Enols. OTTO DIELS (*Annalen*, 1922, 428, 1—55).—An introductory account of this research has already been published (cf. this vol., i, 774).

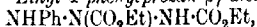
[With SØRENSEN].—The additive product of α -naphthylamine with ethyl azodicarboxylate (cf. A., 1921, i, 280) is readily converted by alcoholic hydrochloric acid into 1-amino-4- $\alpha\beta$ -dicarboethoxyhydrazinonaphthalene hydrochloride,



which undergoes hydrolytic fission in solution in water with the formation of the original additive product, and is reduced by hydriodic acid to 1:4-naphthylenediamine. Sodium 1-amino-2- $\alpha\beta$ -dicarboethoxyhydrazinonaphthalene-4-sulphonate, m. p. 204—210°, the product obtained using sodium naphthionate in place of α -naphthylamine, loses alcohol on treatment with piperidine, giving ethyl 2-keto-6-sulpho-1:3:4-naphthisotriazine-4-carboxylate, m. p. 135°, whilst with concentrated alkali the carboethoxyl group is eliminated, giving 2-keto-1:3:4-naphthisotriazine-6-sulphonic acid, m. p. about 330°. On reduction by sodium amalgam, the hydrazinocompound loses its sulphonic acid group, giving 1-amino-2- $\alpha\beta$ -dicarboethoxyhydrazinonaphthalene, m. p. 147°, which on treatment with hydriodic acid and acetic acid gives 2-methyl- α -naphthiminazole, and on treatment with piperidine or concentrated alkali give, similarly to the sulphonic acids above mentioned, ethyl 2-keto-1:3:4-naphthisotriazine-4-carboxylate, m. p. 272—273°, and 2-keto-1:3:4-naphthisotriazine, m. p. 299°. $\beta\beta$ -Dinaphthylamine and ethyl azodicarboxylate give a small yield of an additive product, $\text{C}_{22}\text{H}_{25}\text{O}_8\text{N}_5$, m. p. 250—252°.

[With MÜLLER].—9-Aminoanthracene combines with ethyl azodicarboxylate, forming 9-amino-10- $\alpha\beta$ -dicarboethoxyhydrazinanthracene, m. p. 199°, which gives a *monoacetyl* derivative, m. p. 277° (decomp.), and a *diacetyl* derivative, m. p. 219—220° (decomp.), and is convertible into anthraquinone by way of 9:10-anthrylenediamine. It also forms an additive product, m. p. 220°, with carbethoxycarbimide.

[With AUBART].—Ethyl α -phenylpropan- $\beta\gamma$ -dicarboxylate,



m. p. 138°, and ethyl α -p-tolylpropan- $\beta\gamma$ -dicarboxylate, m. p. 113°, are formed by the action of ethyl azodicarboxylate on aniline

and *p*-toluidine, respectively. The latter ester decomposes on heating into ethyl hydrazodicarboxylate and an oil from which *p*-toluidine, ethyl *p*-tolylcarbamate, and *p*-azotoluene can be isolated.

[With ECKELMANN.]—Ethyl azodicarboxylate and *p*-xylylidine form 3-amino-6- $\alpha\beta$ -dicarbethoxyhydrazino-*p*-xylene, m. p. 117°, which crystallises from acetonitrile with 1 mol. of solvent, and gives a crystalline hydrochloride and oxalate, m. p. 176°. On treatment with acetic anhydride, it yields an acetyl derivative, m. p. 193°, and with acetic and hydriodic acid it is hydrolysed with the formation of 3:6-diamino-*p*-xylene; sulphuric acid converts the hydrazino-compound into *p*-xyloquinone. *p*-Xylylidine unites with two molecules of the azo-ester, giving a compound, $C_{20}H_{12}O_8N_4$, m. p. 168° (decomp.), from which one molecule of the azo-ester is easily removed with the formation of the preceding hydrazino-compound.

[With KLEINFELLER.]—The azo-ester combines with dimethyl- β -naphthylamine, giving 2-dimethylamino-1- $\alpha\beta$ -dicarbethoxyhydrazinonaphthalene, m. p. 163.5° (perchlorate, m. p. 124°), the constitution of which follows from its formation from 2-amino-1- $\alpha\beta$ -dicarbethoxyhydrazinonaphthalene by methylation. Methyl azodicarboxylate and dimethyl- α -naphthylamine yield 1-dimethylamino-4- $\alpha\beta$ -dicarbomethoxyhydrazinonaphthalene, m. p. 151° (hydrochloride decomposes at 100°), and methyl azodicarboxylate and monomethyl- α -naphthylamine yield 1-methylamino-4- $\alpha\beta$ -dicarbomethoxyhydrazinonaphthalene, m. p. 193°; both the mono- and di-methyl compounds are produced on methylation of 1-amino-4- $\alpha\beta$ -dicarbomethoxyhydrazinonaphthalene, m. p. 203–204°, by means of methyl iodide.

[With WACKERMANN.]—2-Amino-1- $\alpha\beta$ -dicarbomethoxyhydrazinonaphthalene, m. p. 210°, gives a hydrochloride, m. p. 218°, and an acetyl derivative, m. p. 244°, and when treated with piperidine yields a substance, $C_{11}H_8ON_3$, m. p. 315°. On oxidation with hydrogen peroxide, it gives methyl 3-hydroxy- α -naphthatriazole-2:3-dicarboxylate, m. p. 117°.

[With SÖRENSEN.]—1-Amino-4- $\alpha\beta$ -dicarboxymethylamidohydrazinonaphthalene, m. p. 214°, and 1-amino-4- $\alpha\beta$ -dicarboxyethylamidohydrazinonaphthalene, m. p. 213°, are obtained from α -naphthylamine and the appropriate azodicarboxylamide, and can be oxidised to α -naphthaquinone. 2-Amino-1- $\alpha\beta$ -dicarboxymethylamidohydrazinonaphthalene, m. p. 230°, is prepared from β -naphthylamine and azodicarboxymethylamide; on treatment with alkali it yields methyl-1- α -naphthiminazolonecarbamide, m. p. 220–221°, and, on treatment with hydriodic acid and acetic acid, gives α -naphthiminoazolone (1:2-naphthylenecarbamide), m. p. 377°, which was prepared also from 1:2-naphthylenediamine and carbonyl chloride for comparison.

[With KLEINFELLER.]—Azodibenzoyl unites with dimethyl- β -naphthylamine to give an additive product, $C_{26}H_{23}O_2N_3$, m. p. 214–215°, which forms both a hydrochloride and a potassium compound.

[With FULDNER.]—An additive reaction takes place between

ethyl azodicarboxylate and ethyl β -aminocrotonate, but the product is not crystalline. On acid hydrolysis, however, it gives ethyl α -NN'-dicarbethoxyhydrazinoacetoacetate, m. p. 75°. Ethyl β -amino- α -NN'-dicarbomethoxyhydrazinocrotonate has m. p. 140°, and its hydrolysis product, ethyl α -NN'-dicarbomethoxyhydrazinoacetoacetate, has m. p. 113°.

Ethyl acetoacetate reacts directly with ethyl azodicarboxylate, giving ethyl α -NN'-dicarbethoxyhydrazinoacetoacetate, and acetylacetone gives β -dicarbethoxyhydrazinoacetylacetone, m. p. 123°, and β -dicarbomethoxyhydrazinoacetylacetone, m. p. 120°, on treatment with the appropriate azo-ester.

C. K. I.

Catalytic Preparation of Azobenzene and Aniline. II. C. O. HENKE and O. W. BROWN (*J. Physical Chem.*, 1922, 26, 631—638; cf. this vol., i, 586).—A continuation of work previously published on the reduction of nitrobenzene in the presence of metallic catalysts. The method of procedure is the same as that previously adopted, and in the present work the effect of using thallium and gold as catalysts has been investigated. Thallium prepared from thallic oxide at 260° is shown to be an excellent catalyst for the reduction of nitrobenzene to azobenzene. With a rate of flow of 4.1 grams of nitrobenzene per hour with a 13% excess of hydrogen a material yield of 90.2% of azobenzene and 4.3% of aniline is obtained. The activity of the thallium catalyst decreases very rapidly with use, and this is probably caused by it melting and running together. Gold has a high catalytic activity for producing aniline which decreases with use. With this metal as catalyst, the yield of aniline at 355° is almost quantitative.

J. F. S.

The Reaction between Azobenzene Hydrochloride and Aromatic Hydrocarbons. II. RUDOLF PUMMERER, JOSEF BINAPFL, KARL BITTNER, and KARL SCHUEGRAF (*Ber.*, 1922, 55, [B], 3095—3104).—It has been shown previously (this vol., i, 24) that azobenzene reacts with benzene in the presence of aluminium chloride and hydrogen chloride to give *p*-aminodiphenyl as main product. The examination of the change has been extended, whereby it is found that the *p*-aminophenyl residue can be conveniently introduced into many aromatic compounds by the help of azobenzene.

In the previous communication (*loc. cit.*), the carbonium formula has been suggested tentatively for azobenzene hydrochloride, $\left[\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{C}_6\text{H}_4 \right]^{\text{H}} \text{Cl}$. An analogy between the compound and triphenylcarbonium chloride is found in the observation that they yield dark brown solutions in phenol or *p*-cresol, whereas only a slight deepening of colour is observed in other solvents. Benzylideneaniline and benzophenoneanil, which are constitutionally closely related to azobenzene, do not show this colour change with phenol and hydrogen chloride; they do not act as phenylating agents in the Friedel-Crafts' reaction.

The reaction between azobenzene hydrochloride and toluene in

the presence of aluminium chloride is more vigorous than that observed with benzene, so that in order to avoid the hydrogenating action of toluene and aluminium chloride the temperature should not be allowed to rise above 10–15°. The product consists of a mixture of the hydrochlorides of 4'-amino-4-methyldiphenyl, benzidine, aniline, and possibly semidine bases from which the former is most conveniently separated by fractional sublimation at 190–200°/20 mm. (the temperature being that of the bath). 4'-Amino-4-methyldiphenyl, $C_6H_5Me \cdot C_6H_4 \cdot NH_2$, has m. p. 98.5–99°, in agreement with the observations of Kliegl and Huber (A., 1920, i, 835).

o-Azotoluene hydrochloride is transformed by benzene in the presence of aluminium chloride into the hydrochloride of 4-amino-3-methyldiphenyl which is isolated from the crude product of the reaction by fractional sublimation in a vacuum. 4-Amino-3-methyldiphenyl, $C_6H_5 \cdot C_6H_3Me \cdot NH_2$, is a pale yellow, viscous liquid, b. p. 190–191°/15 mm., which does not solidify when placed in a freezing mixture. Its acetyl derivative forms colourless crystals, m. p. 165.5°, whereas the benzylidene compound crystallises in yellow leaflets, m. p. 108.5°.

The action of naphthalene on azobenzene hydrochloride in the presence of aluminium chloride has been examined in carbon disulphide solution; the yields of the products and the success of the experiments depend greatly on the purity of the reagents. The crude product is a mixture of the hydrochlorides of benzidine and *p*- α -naphthylaniline with naphthylazobenzene and dinaphthylazobenzene (the azo-compounds have only been examined qualitatively up to the present). *p*- α -Naphthylaniline, $C_{10}H_7 \cdot C_6H_4 \cdot NH_2$, crystallises in colourless leaflets, m. p. 94–95°; it yields a benzylidene compound, pale yellow crystals, m. p. 164.5°.

Azobenzene hydrochloride and diphenyl yield 1-phenyl-4-*p*-aminophenylbenzene, $C_6H_4Ph \cdot C_6H_4 \cdot NH_2$, silvery leaflets, m. p. 198° (in an atmosphere of carbon dioxide). The base yields solid yellow diazonium salts which are relatively very stable and couple with R-salt with the formation of a bluish-red dye. The diazonium sulphate is deaminated by an alkaline solution of sodium stannite with the formation of 1 : 4-diphenylbenzene, m. p. 209°. H. W.

Attempts to Prepare Red Sulphide Dyes. II. Mercaptan Derivatives of Azo-dyes. EDWIN ROY WATSON and SIKHIBHUSHAN DUTT (T., 1922, 121, 2414–2419).

Some Arylazoglyoxalines. FRANK LEE PYMAN and LAURENCE BARNETT TIMMIS (*J. Soc. Dyers and Col.*, 1922, 38, 269–272).—The arylazoglyoxalines of the type $\begin{matrix} CH \cdot NH \\ | \\ CH \cdots N \end{matrix} > C \cdot N \cdot NR$,

where R is an aryl group, formed by coupling glyoxaline with diazonium salts in alkaline solution, are produced in widely varying yield according to whether the diazonium compound contains an ortho-substituent or not. Thus the yield of 2-benzeneazoglyoxaline is 74% of the theory, 2-*p*-bromobenzeneazoglyoxaline

85%, 2-*p*-tolueneazoglyoxaline 84%, 2-*p*-ethoxybenzeneazoglyoxaline 64%, and 2-*p*-sulphobenzeneazoglyoxaline 52%, as against 2-*o*-tolueneazoglyoxaline 26%, and 2-*o*-methoxybenzeneazoglyoxaline 10%. The yields of 2-aminoglyoxaline, formed by reduction with stannous chloride of such arylazoglyoxalines as have a para-substituent in the benzene ring also vary widely, ranging from only 15% from 2-*p*-tolueneazoglyoxaline to 26% from the *p*-ethoxy-compound, 43% from the *p*-sulpho-compound, and 56% from the *p*-bromo-compound. Those not containing a para-substituent give under similar treatment 65–75% yields of diaminophenylglyoxalines. These diamines cannot be tetrazotised, as the glyoxaline amino-group does not react normally with nitrous acid. The arylazoglyoxalines dye wool brownish-yellow shades, but the colours are not fast. 2-*o*-Methoxybenzeneazoglyoxaline forms orange prisms, m. p. 161° (corr.), which on reduction with stannous chloride yield 2:4'-diamino-4-m-methoxyphenylglyoxaline, isolated as its dihydrochloride, white needles, m. p. 268° (corr., decomp.). It also forms a picrate, m. p. 202° (corr.), and a sparingly soluble sulphate. 2-*p*-Ethoxybenzeneazoglyoxaline forms brownish-red plates, m. p. 216° (corr.). G. F. M.

The Triazo-group. XXII. Cinnamic Acid Chlorohydrin and its Conversion into α -Triazo- β -hydroxy- β -phenylpropionic Acid. MARTIN ONSLOW FORSTER and WILLIAM BRISTOW SAVILLE (T., 1922, 121, 2595–2601).

The Coagulation of Proteins by Heat. W. W. LEPESCHKIN (Biochem. J., 1922, 16, 678–701).—The coefficient of denaturation is equal to 1.5–2.5 per one degree. From the study of the influence of alkalis and acids on denaturation, it is concluded that denaturation is a weak hydrolysis of protein. The denaturation of protein is increased by the presence of salts—potassium thiocyanate has a greater effect than potassium sulphate and potassium chlorate takes the middle position, that is, the effect depends on the lyotropic properties of the salts. The coagulation of denaturated protein proceeds at a certain temperature considerably more rapidly than the denaturation at the same temperature if the protein solution contains a sufficiently large amount of salt. The temperature coefficient of coagulation of denaturated albumin is greater than that of arsenic trisulphide or lecithin, but is nearer to that of lecithin, which occupies an intermediate position between a suspensoid and an emulsoid. Acid strongly increases and alkali strongly diminishes the coagulation rate of denaturated albumin. The increase, however, is not proportionate to the concentration of the hydrogen or hydroxyl ions, and is evidently due to the formation of acid and alkali compounds of the denaturated protein. The colloidal state of the acid compounds is nearer to that of a typical suspensoid, whilst that of alkali compounds is nearer to that of an emulsoid. The colloidal state of the acid compounds of denaturated albumin is not identical with that of the denaturated acid compounds of native albumin formed in the presence of the same concentration of acid. The coagulation velocity of denaturated albumin formed

in the presence of potassium chloride is greater than the coagulation velocity of denaturated albumin formed when the salt is not present. Serum-albumin and egg-albumin are altered after prolonged dialysis in such a manner that after denaturation they show a greater susceptibility to salts than before. This is not in agreement with the observations of Pauli and Handovsky. The action of the kations on the velocity of coagulation of denaturated albumin is not proportional to their valency; trivalent kations produce an acceleration which is almost the same as that produced by univalent ions, and consequently the coagulation of denaturated albumin cannot be regarded simply as a process of electrical discharge of protein particles by the ions, but must be held also to be a chemical phenomenon.

S. S. Z.

Adsorption of Proteins, Ferments, Toxins, and Sera by Aluminium Hydroxide. M. A. RAKUSIN (*Z. Immunol.*, 1922, 34, 155—193; from *Chem. Zentr.*, 1922, iii, 644).—Albumin in egg-white solution is separated into two components by anhydrous aluminium hydroxide. The two components differ in optical rotatory power. Casein is adsorbed without separation. Chondrin is separated from chondroitin-sulphuric acid which remains in solution whilst the colloidal chondrin residue is irreversibly adsorbed. Pepsin, trypsin, and pancreatin are partly adsorbed. Papain in aqueous solution is not absorbed. Diastase is decomposed. Koch tuberculin and Denys tuberculin may be distinguished through their adsorption by aluminium hydroxide. Pöhl spermin, diphtheria antitoxin, and pepsin-fibrin peptone all undergo separation into simpler components on treatment with aluminium hydroxide.

G. W. R.

The Nitrogen Distribution in Bence Jones's Protein. A New Colorimetric Method for the Estimation of Tryptophan in Protein. ERY LÜSCHER (*Biochem. J.*, 1922, 16, 556—563).—Bence Jones's protein differs from all the proteins analysed up to the present time, not only in its physical behaviour, but also in its nitrogen distribution as determined by Van Slyke's method. There is, however, some evidence that the same protein appears in the urine in all cases of Bence Jones's proteinuria.

The author proposes to use benzaldehyde instead of formaldehyde in Fürth's and Sieben's colorimetric method for the estimation of tryptophan (*A.*, 1921, ii, 71).

S. S. Z.

The Content of the Proteins of the Lens in Histidine, Arginine, and Lysine. A. JESS (*Z. physiol. Chem.*, 1922, 122, 160—165).—The three proteins in the lens, α -crystallin, β -crystallin, and albumoid contain, respectively, 3.8%, 2.6%, and 2.7% of histidine, 8.0%, 7.5%, and 10.3% of arginine, and 3.7%, 4.6%, and 3.8% of lysine.

W. O. K.

The Physical Chemistry of Hæmoglobin in Blood. W. E. L. BROWN and A. V. HILL (*Arch. Néerland. physiol.*, 1922, 7, 174—178).—It has been suggested that hæmoglobin is polymerised by salts, and that it combines with oxygen according to the equation

$\text{Hb}_n + n\text{O}_2 \rightleftharpoons (\text{HbO}_2)_n$. This view is supported by measurements of the heat of reaction of hæmoglobin with oxygen. W. O. K.

Nucleic Acid-Protein Compounds. H. STEUDEL and E. PEISER (*Z. physiol. Chem.*, 1922, 122, 298—306).—In order to elucidate the structure of nucleoproteins, presumably salts of nucleic acid and protein, salts of this type have been prepared from clupein and guanylic acid, from clupein and yeast-nucleic acid, and from clupein and eosin, and their content in phosphorus and in nitrogen has been determined. W. O. K.

The Diastatic Action of Albumoses and Amino-acids. W. BIEDERMANN (*Arch. Néerland. physiol.*, 1922, 7, 151—156).—If blood-fibrin is heated with water in a sealed tube at $160\text{--}170^\circ$, the resulting solution after filtration shows a definite diastatic action on starch. This does not take place in the absence of oxygen or of sodium chloride. Certain amino-acids, for example, glycine and leucine, have a similar action, and with these, too, the presence of oxygen and of salt ions is necessary. W. O. K.

Invertase. III. RICHARD WILLSTÄTTER, JOHANNA GRASER, and RICHARD KUHN (*Z. physiol. Chem.*, 1922, 123, 1—78; cf. A., 1921, i, 823; this vol., i, 598).—Preparations of autolysed yeast change with age in such a way that the invertase becomes practically completely precipitable by lead acetate. This, in combination with the methods previously used (*loc. cit.*)—particularly adsorption with aluminium hydroxide and dialysis—gives a means of obtaining extremely active invertase preparations. The precipitation by lead acetate is affected also by other factors such as incidental substances present in the invertase solution, particularly phosphates. The phosphorous content of these very highly active invertase preparations is very low.

The activity of invertase appears to be independent of the other compounds which accompany it, and also independent of the state of aggregation. Incidental impurities are, however, important in this respect, that the very pure preparations are much less stable. They can be protected by the addition of, for example, calcium chloride or yeast-gum.

Purified invertase has an optimum activity at P_{H} 4.6. Experiments carried out on the kinetics of the reaction indicate that it is unimolecular. W. O. K.

The Phosphorus Content of Purified Saccharase Preparations. H. VON EULER and O. SVANBERG (*Arkiv Kem. min. Geol.*, 1922, 8, No. 12, 1—13).—By estimating the concentration of silver ions electrometrically, the dissociation constants of the silver salts of the following acids have been determined: cysteine, 0.89×10^{-6} ; combined nucleic acid, 0.28×10^{-7} ; guanylic acid, 4.2×10^{-6} ; inosic acid, 9.3×10^{-8} ; adenylic acid, 1.85×10^{-3} ; guanosine, 1×10^{-4} ; adenosine, 5.0×10^{-8} ; caffeine, 4.9×10^{-2} ; guanidine, about 10^{-4} ; uric acid, about 10^{-4} . These may be compared with the value of 0.87×10^{-6} obtained for a highly purified saccharase. It is probable that the presence in the saccharase molecule of

components of the nature of nucleic acids may explain the poisoning of the enzyme by silver salts, as these acids have a strong affinity for silver ions.

Purified saccharose solutions after exhaustive dialysis leave an ash which can be completely accounted for by the phosphoric acid present, indicating the absence of any corresponding metal as base.

W. O. K.

Enzyme Chemistry. HANS VON EULER and KARL MYRABÄCK (*Arkiv Kem. Min. Geol.*, 1922, 8, No. 17, 1--15).—By acting on a purified saccharase solution with *Bacillus macerans*, or with the digestive enzyme from *Helix pomatia*, and then dialysing, the authors have obtained a preparation of only slightly diminished activity, but with a much smaller dry residue. The activity of the material left behind was therefore much increased. The enzyme from *Aspergillus oryzae* and also Taka diastase gave similar results.

In presence of phenol, dextrose is more easily esterified by phosphate under the influence of yeast than is maltose. In the presence of toluene, the initial fermentation of dextrose and maltose is inhibited much more than that of saccharose.

W. O. K.

Reductases. I. Some Conditions of the Activity of Starch Reductase. I. A. SMORODINCEV (*Z. physiol. Chem.*, 1922, 123, 130--144).—Estimations made of the amount of nitrite produced from nitrate by an extract of potatoes in presence of acetaldehyde indicate an increase in the reaction with increase of the amount of ferment used, but not nearly so marked an increase with increasing amount of aldehyde. Neither formaldehyde nor vanillin is so efficient as acetaldehyde. With acetaldehyde, the reaction ceases after thirty to sixty minutes. Atmospheric oxygen does not appear to be harmful, and very dilute acid is favourable, although greater concentrations markedly retard the reaction.

W. O. K.

Synthesis of Aromatic Arsinic Acids. HEINRICH BART (*Annalen*, 1922, 429, 55--103).—The method of preparing arylarsinic acids by the interaction of aromatic diazonium solutions with acid or alkaline arsenite solutions, which has been widely used of recent years, was nevertheless originated by the author (D.R.P. 250264).

Details are given for the preparation of a number of arylarsinic acids certain of which are new: phenylarsinic acid, *o*-tolylarsinic acid, *m*-tolylarsinic acid, *p*-tolylarsinic acid, *p*-ethoxyphenylarsinic acid, *p*-acetylaminophenylarsinic acid, *o*-chlorophenylarsinic acid, needles, m. p. 181°, *m*-chlorophenylarsinic acid, m. p. 175°, *p*-chlorophenylarsinic acid, *o*-carboxyphenylarsinic acid, *m*-carboxyphenylarsinic acid, needles which lose water at 250°, *p*-carboxyphenylarsinic acid, *p*-phenylenediarsinic acid, *o*-hydroxyphenylarsinic acid, m. p. 191°, *p*-hydroxyphenylarsinic acid, *o*-nitrophenylarsinic acid, needles, m. p. 233°, *m*-nitrophenylarsinic acid, needles, m. p. about 200°, *p*-nitrophenylarsinic acid, m. p. above 300° (decomp.), *op*-dinrophenylarsinic acid, 5-nitro-2-hydroxyphenylarsinic acid, decotap.

250°, *o*-nitro-*p*-hydroxyphenylarsinic acid, m. p. 228°, and *m*-nitro-*p*-hydroxyphenylarsinic acid.

Diphenylarsinic acid, m. p. 178°, is obtained from benzene-diazonium chloride and phenylarsine oxide. *p*-Nitrophenylarsenious acid is obtained by reduction of *p*-nitrophenylarsinic acid; on treatment with a diazo-solution prepared from *p*-nitroaniline it yields *di-p*-nitrophenylarsinic acid, m. p. 278°. C. K. I.

Synthesis of Aromatic Arsinic Acids by the Interaction of isoDiazo-compounds with the Arsenite-ion. HEINRICH BART (*Annalen*, 1922, 429, 103—113).—The same end-product is obtained if in the general reaction referred to in the preceding abstract the diazonium solution is replaced by alkaline isodiazotates. Details are given for the preparation by this method of the following substances: *o*-nitrophenylarsinic acid, *m*-nitrophenylarsinic acid, *p*-nitrophenylarsinic acid, phenylarsinic acid, *o*-carboxyphenylarsinic acid, and *p*-carboxyphenylarsinic acid. C. K. I.

Two New Syntheses of *mm'*-Diamino-*pp'*-dihydroxyarsenobenzene (Salvarsan Base). HEINRICH BART (*Annalen*, 1922, 429, 113—122).—The first synthesis consists in converting 3-amino-6-hydroxyazobenzene into 4-hydroxy-3-benzeneazophenylarsinic acid (cf. preceding abstracts) which on reduction yields the required substance and two molecules of aniline.

The starting point of the second synthesis is *p*-nitro-*o*-aminophenol, which is condensed with ethyl chloroformate and the urethane, m. p. 208°, reduced to give *p*-amino-*o*-carbethoxyaminophenol. The latter is readily converted into *m*-carbethoxyamino-*p*-hydroxyphenylarsinic acid, m. p. 200°, which on reduction gives the urethane of the required base. C. K. I.

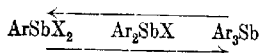
The Colloidal Properties of Arsphenamine [Salvarsan] and Allied Products. GEORGE W. RAIZISS and JOSEPH L. GAVRON (*J. Pharm. Expt. Ther.*, 1922, 20, 163—179).—Experiments on the dialysis of 3:3'-diamino-4:4'-dihydroxyarsenobenzene hydrochloride (salvarsan) through a parchment membrane indicate that the solution in water is of a colloidal nature as it diffuses through the membrane but slightly, whilst in methyl-alcoholic solution it diffuses more readily. The disodium salt diffuses about four times as quickly as the hydrochloride. By dialysing silver sodium salvarsan, it is found that the arsenic diffuses to the extent of about 26% in thirty-six hours, whilst the silver remains completely behind. Similar results have been found with gold sodium salvarsan. This is taken to indicate that in these compounds the silver or gold is probably in a colloidal form and not chemically combined with the arsenic organic compound. W. O. K.

The Sulphur Content of Arsphenamine [Salvarsan] and its Relation to the Mode of Synthesis and Toxicity. III. WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1922, 44, 2334—2342; cf. A., 1921, i, 370; this vol., i, 186, 601; Fargher and Pyman, T., 1920, 117, 370).—It is shown that in reducing 3-nitro-4-hydroxyphenylarsinic acid to salvarsan the formation of relatively

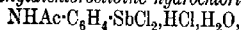
toxic products with a high sulphur content is not due to impurities in the commercial sodium hyposulphite. The salvarsan base is fairly uniform in regard to toxicity and sulphur content irrespective of the period of formation during the reduction. Amino-hydroxyarseno-compounds in general contain the fewest sulphur atoms when prepared from the amino-acids. Fixation of the hydroxyl hydrogen atom in the nitrohydroxyarsinic acids tends to make the hyposulphite reduction abnormal, and the products, when they can be isolated, contain more sulphur than analogous substances prepared without fixation of this hydrogen atom. The hydroxyl hydrogen ortho to the nitro-group seems to play an important rôle in the formation of arseno-compounds of the type under consideration. The sulphonic acid group found in certain samples of arsphenamine probably enters the ring by way of the nitrogen atom with the intermediate formation of a sulphamic acid.

Compounds described are: 3-nitro-4-methoxyphenylarsinic acid; 3-nitro-4-hydroxy-5-methylphenylarsinic acid; 4-methoxy-5-methylphenylarsinic acid and its 3-nitro-derivative; 3-nitro-4-carbomethoxyphenylarsinic acid; 3-nitro-4:6-dimethoxyphenylarsinic acid; 3-acetyl-amino-4-methoxyphenylarsinic acid; 3:3'-diamino-4:4'-dimethoxyarsenobenzene dihydrochloride; 3:3'-diamino-4:4'-dihydroxy-5:5'-dimethylarsenobenzene dihydrochloride; and 3:3'-diamino-4:4':6:6'-tetramethoxyarsenobenzene dihydrochloride. W. G.

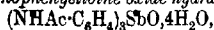
Aromatic Antimony Compounds. HANS SCHMIDT (*Annalen*, 1922, 429, 123—152).—VI. *New Reciprocal Interconversions of Mono-, Di-, and Tri-arylantimony Compounds.*—The examples given in this paper show that it is possible to realise the reciprocal interconversion, in the sense of the formulæ following, of mono-, di-, and tri-aryl derivatives of tervalent antimony.



p-Acetylaminophenyldichlorostibine hydrochloride,



is obtained as colourless crystals, sintering at 125°, by reducing *p*-acetylaminophenylantimonious acid with stannous chloride. It decomposes on keeping, but free *p*-acetylaminophenyldichlorostibine, which is obtained from it by rubbing with methyl alcohol, is quite stable, forming colourless crystals, m. p. 200°. This substance on treatment with ammonia yields *p*-acetylaminophenylstibinous oxide, $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SbO}\cdot\text{H}_2\text{O}$, sinters at 180°, which on boiling with methyl alcohol is converted into tri-*p*-acetylaminophenylstibine. This crystallises from methyl alcohol as needles, with 0.5H₂O, sintering at 205°, m. p. 270°, from acetone in an anhydrous form, m. p. 268°, and from aqueous acetone in a form containing (2/3)H₂O, which sinters at 225°. On oxidation with hydrogen peroxide it yields tri-*p*-acetylaminophenylstibine oxide hydrate,



m. p. 200°.

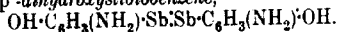
Tri-*p*-acetylaminotriphenylstibine, on treatment with methyl alcoholic hydrogen chloride, passes into *di-p*-acetylaminophenylchlorostibine hydrochloride, m. p. 135° , which yields *di-p*-acetylaminophenylhydroxystibine, $(\text{NHAc}\cdot\text{C}_6\text{H}_4)_2\text{Sb}\cdot\text{OH}\cdot 1\cdot5\text{H}_2\text{O}$, m. p. about 130° , on treatment with methyl-alcoholic sodium hydroxide. Any of these compounds on oxidation with hydrogen peroxide under appropriate conditions gives *di-p*-acetylaminophenylstibinic acid, $(\text{NHAc}\cdot\text{C}_6\text{H}_4)_2\text{SbO}\cdot\text{OH}\cdot 3\text{H}_2\text{O}$, which sinters and turns brown at 235° .

Diphenylacetoxystibine, needles, m. p. 132° , is produced from triphenylstibine when the latter is heated with methyl alcoholic hydrochloric acid and the product obtained after making alkaline is crystallised from acetic acid. Triphenylstibine diacetate, $\text{Ph}_3\text{Sb}(\text{OAc})_2$, m. p. 215° , is formed when triphenylstibine is oxidised in acetone solution with hydrogen peroxide and the product treated with acetic acid.

Derivatives of diphenylhydroxystibine readily pass on treatment with such reagents as formic, acetic, and hydrochloric acids into derivatives of phenyldihydroxystibine.

VII. *p*-Amino-, *p*-Hydroxy-, and *p*-Ethoxy-phenylantimonious Acids. — *p*-Aminophenylstibinic acid, $3\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SbO}(\text{OH})_2\cdot 4\text{H}_2\text{O}$, is obtained by hydrolysis of *p*-acetylaminostibinic acid, and on treatment with hydrochloric acid gives *p*-aminophenyltetrachlorostibine hydrochloride, $\text{NH}_2\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{SbCl}_4\cdot 1\cdot5\text{H}_2\text{O}$, m. p. 155° (decomp.). *p*-Hydroxyphenylstibinic acid, $3\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SbO}(\text{OH})_2\cdot 6\text{H}_2\text{O}$, is prepared from the amino-compound by the diazo-reaction, and gives a characteristic pyridine double salt, m. p. 176° . *p*-Ethoxyphenylstibinic acid, $3\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{SbO}(\text{OH})_2\cdot 2\text{H}_2\text{O}$, is obtained by the diazo-reaction from *p*-phenetidine; it forms a colourless powder which turns dark but does not melt at 270° .

VIII. *mm'*-Diamino-*pp'*-dihydroxystibiobenzene. — *m*-Nitro-*p*-hydroxyphenylstibinic acid on reduction by stannous chloride gives *m*-amino-*p*-hydroxyphenyldichlorostibine hydrochloride, m. p. 165 – 170° , which on further reduction with hypophosphite yields *mm'*-diamino-*pp'*-dihydroxystibiobenzene,



C. K. I.

Organo-metallic Compounds. III. The Mechanism of the Wurtz-Fittig Synthesis. HANS HEINRICH SCHLUBACH and EDUARD C. GOES (*Ber.*, 1922, 55, [B], 2889–2902; cf. A., 1920, i, 19).—The extension of the observations of the action of carbon monoxide on sodium alkyls (Schlubach, *loc. cit.*) to the Wurtz-Fittig synthesis leads the authors to the following general conception of the course of the latter change. The primary phase consists in the transformation of alkyl haloid into the corresponding radicals: $\text{R}\cdot\text{Hal} + \text{Na} \rightarrow \text{R}\cdot + \text{NaHal}$. In the second phase, the radical may combine with sodium to yield the sodium alkyl, RNa , may become polymerised to the saturated hydrocarbon, $\text{R}\cdot\text{R}\cdot$, or, if a hydrogen atom is readily displaced, may become transformed into $\text{R}\cdot\text{H}$ and $\text{R}\cdot\text{H}$. In the third phase, the sodium alkyl

may react with alkyl haloid to give a saturated hydrocarbon, $RNa + RHal \rightarrow R \cdot R + NaHal$, or the transformation to R_{-H} and R_{+H} , may again occur. In the aliphatic series from ethyl upwards, the last is the main change. With methyl, on the other hand, this change is not observed, the main result being the union of the alkyl radicles with production of ethane. With increasing length of the aliphatic hydrocarbon chain, the transformation becomes less marked and the union of the radicles more pronounced, so that (with cetyl bromide, for example) good yields of saturated hydrocarbons are ultimately obtained. In the aromatic series, the formation of sodium aryls takes place smoothly; the slight reactivity of aromatically combined halogen makes the further production of compounds, $R \cdot R$, difficult, whereas it is easy with aliphatic haloids. Complications of the reaction which are due to the solvent can also arise. Thus sodium ethyl reacts with diethyl ether to yield ethylene and ethane in accordance with the equation $Et \cdot O \cdot Et + NaEt = NaOEt + C_2H_4 + C_2H_6$. With benzene and its homologues, a reaction can also occur: $R \cdot Na + R'H = R \cdot H + R'Na$ (cf. Schorigin, A., 1910, i, 547).

The characteristic phenomena on which the hypothesis of the pre-existence of free radicles is based are found, not only with sodium alkyls, but also with many organometallic compounds. The reducing properties of the organometallic derivatives of zinc and magnesium are well known, and Späth (A., 1914, i, 1) has observed that the same anomalous products are obtained when alkyl haloids react with Grignard's reagents and with sodium alkyls. It therefore appears probable that free radicles are also formed in this case; Hess's recent assumption of the existence of magnesium hydrogen haloids (A., 1921, i, 777) appears to be unnecessary.

Blue products are invariably produced during the course of a Wurtz-Fittig synthesis. These have been considered by Schorigin (A., 1908, i, 866) to be entirely inorganic. With this view the authors concur, since examination of the product from benzyl chloride and sodium shows it to be discoloured sodium chloride.

When bromobenzene is added gradually to sodium beneath dry benzene in an atmosphere of carbon monoxide, absorption of the gas begins after about two hours and is complete within about eight days. The products are benzoic acid, diphenyl, benzophenone, and triphenylcarbinol. Ethyl bromide, sodium, and carbon monoxide in the presence of ethyl ether give ethylene, diethyl ketone, and triethylcarbinol.

The hope of isolating the cetyl radicle has led the authors to study the action of sodium on cetyl bromide in the presence of a little ether; carbon monoxide is not absorbed during the change, and the crystals of metallic lustre which separate do not yield any organic substance when treated with water. At a somewhat higher temperature, dicetyl, m. p. 70.5° , is obtained in 88% yield.

Definite evidence of the transitory existence of sodium alkyls in the Wurtz-Fittig synthesis is found in the observation that benzyl chloride and sodium give an immediate wine-red coloration

(benzyl sodium in contrast to the other alkyl sodium compounds is red in colour) which gradually passes to the customary dark blue.

A mixture of equivalent quantities of ethyl bromide and bromobenzene is converted by sodium in an atmosphere of carbon monoxide into benzoic acid, benzophenone, and triphenylcarbinol; it thus appears that under similar conditions sodium phenyl is produced more readily than sodium ethyl, and that unchanged ethyl bromide reacts more readily than bromobenzene with sodium phenyl. In the main, the change occurs through the phases: $\text{PhBr} + 2\text{Na} \rightarrow \text{PhNa} + \text{NaBr}$ and $\text{PhNa} + \text{EtBr} \rightarrow \text{PhEt} + \text{NaBr}$.

The tendency of the radicles to saturate their free valency is evidenced not only by polymerisation, but also by loss of hydrogen; as a general rule, a second radicle plays the part of acceptor (for example, $2\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$), but this rôle may also be played by a readily oxidisable material. Thus sodium ethyl and benzaldehyde, when heated in the presence of toluene, give ethylene, benzyl alcohol, and phenylethylcarbinol (cf. also Schorigin, A., 1908, i, 881).
H. W.

The Preparation and Properties of Organic Stanno- and Stanni-chlorides. V. The Salts of certain Special Bases. J. G. F. DRUCE (*Chem. News*, 1922, 125, 265—267; cf. this vol., i, 639).—*Hydroxylamine stannichloride*, $(\text{NH}_2\text{OH})_2\text{H}_2\text{SnCl}_6$, forms a microcrystalline deposit from dilute hydrochloric acid, soluble in cold water, but hydrolysed in the hot. *5-Aminoquinoline stannichloride*, $\text{C}_9\text{H}_8\text{N}_2\text{H}_2\text{SnCl}_6$, forms pale yellow prisms, m. p. 160°; *5-aminoquinoline stannichloride*, $\text{C}_9\text{H}_8\text{N}_2\text{H}_2\text{SnCl}_6$, forms orange crystals, m. p. 242°; these give cloudy solutions in water. *6-Amino-2-methylquinoline stannochloride*, $\text{C}_{10}\text{H}_{10}\text{N}_2\text{H}_2\text{SnCl}_6$, forms felted masses of deliquescent, white crystals giving a clear solution in cold water; it decomposes at 180°. *6-Amino-2-methylquinoline stannichloride*, $\text{C}_{10}\text{H}_{10}\text{N}_2\text{H}_2\text{SnCl}_6$, forms nacreous plates, m. p. 224—228° (decomp.), soluble in cold water to a clear solution which slowly deposits hydrated stannic oxide. *isoQuinoline stannichloride*, $(\text{C}_9\text{H}_7\text{N})_2\text{H}_2\text{SnCl}_6$, forms almost colourless, prismatic crystals, m. p. 265°, soluble in cold but hydrolysed by hot water.
E. H. R.

Physiological Chemistry.

Influence of Hydrogen Sulphide on Respiration. H. W. HAGGARD and Y. HENDERSON (*Amer. J. Physiol.*, 1922, 61, 289—297).—An atmosphere containing 0.05% of hydrogen sulphide causes the death, from lung cedema, of dogs only after many hours' continued breathing, whereas a concentration of 0.1% causes death in fifteen to twenty minutes. Estimations of the carbon dioxide and oxygen content of the blood and its carbon dioxide combining power indicate that hydrogen sulphide in sufficient

amount stimulates the respiration through an action on the vagi. As a result, carbon dioxide is removed from the blood and the hydrogen-ion concentration of the blood lowered until alkalosis of sufficient degree is produced, when the stimulating action of the hydrogen sulphide is counteracted and an apnoea follows, before and during which the hydrogen sulphide of the blood is oxidised. Small amounts of hydrogen sulphide are generally without perceptible effect on the respiratory centre, whereas larger amounts paralyse respiration.

CHEMICAL ABSTRACTS.

Relation between Changes of Temperature and Consumption of Oxygen by Cold-blooded Animals. M. N. J. DIRKEN (*Arch. Néerland. physiol.*, 1922, 7, 126—131).—Measurements of the oxygen consumption of cockroaches (*Periplaneta americana*) show an increase with rise of temperature, the temperature coefficient being 4.3 between 10° and 20° and 1.7 between 20° and 30°.

W. O. K.

Gas and Electrolyte Equilibria in Blood. I. Technique for Collection and Analysis of Blood, and for its Saturation with Gas Mixtures of Known Composition. J. H. AUSTIN, G. E. CULLEN, A. B. HASTINGS, F. C. MCLEAN, J. P. PETERS, and D. D. VAN SLYKE (*J. Biol. Chem.*, 1922, 54, 121—147).—The authors describe a technique for the preliminary treatment of blood by means of which it is hoped, in conjunction with analytical methods previously described (Van Slyke and Stadie, this vol., ii, 78), to obtain accurate quantitative data concerning the various reactions involved (cf. Henderson, A., 1921, i, 473) in the respiratory changes in blood. The main features of the technique are two methods for saturating the blood with gas mixtures whereby changes in the gaseous equilibrium, due to the changes in pressure and temperature which result when the tonometer is removed from the bath, may be avoided. In the first method, the tonometer consists of two chambers connected by means of a rubber tube. When saturation is complete, the blood is run into the smaller chamber, the rubber connexion is closed at two points by means of clamps, and the chambers are then separated by cutting the rubber at a point between the two clamps. Before removing the smaller chamber from the bath, the gases are displaced from it by mercury from a levelling bulb. In the second method, analysis of the gas phase is avoided by calculating the amount of carbon dioxide and oxygen taken from it by the blood during saturation. The whole technique, from the drawing of the blood to the analysis of the blood gases, is described in detail in the original, and a diagram is provided illustrating the apparatus employed. Equations necessary for the calculations involved are also developed. E. S.

Gas and Electrolyte Equilibria in Blood. II. The Reversibility of the Effects of Changes in Carbon Dioxide and Oxygen Tensions on the Carbon Dioxide Content of De-fibrinated Horse Blood. JOHN P. PETERS, GLENN E. CULLEN, and J. HAROLD AUSTIN (*J. Biol. Chem.*, 1922, 54, 149—152).—No irreversible changes in the carbon dioxide capacity of defibrinated

horse blood are produced by reducing the carbon dioxide or oxygen tension to 15 mm. The reduction of the carbon dioxide capacity of dog's blood by similar treatment is probably due, as Evans (this vol., i, 890) suggests, to the formation of acid, which occurs rapidly in dog's blood. E. S.

Calcium in the Blood. P. VAN PAASSEN (*Nederland. Tijdschr. Geneeskunde*, 1921, 65, ii, 1162—1171).—The concentration of the calcium-ions, on which the effect of the calcium content of the blood depends, in serum is given by the expression $K\frac{[H^+]}{[HCO_3^-]}$ where $K=350$. Thus, when the concentration of the hydrogen-ions is constant in the blood, a change in the concentration of calcium ions can be brought about only by increasing or decreasing the concentration of the hydrogen carbonate-ions.

CHEMICAL ABSTRACTS.

The Blood-sugar Content of Capillary Blood as Compared with that of Venous Blood. ISAAC NEUWIRTH and I. S. KLEINER (*J. Lab. Clin. Med.*, 1922, 7, 495—497).—In twenty individuals the capillary blood sugar was found to parallel the venous blood sugar. The average of all twenty capillary figures for blood-sugar is 0.136% as against 0.130% for the venous. The slight difference in this sense would be expected. The blood-sugar estimations were made by the Kleiner micro-method.

CHEMICAL ABSTRACTS.

Blood-sugar. A. STASIAK (*Z. physiol. Chem.*, 1922, 123, 104—115).—Dog's blood shows an increase of its sugar content if it be boiled with 2% hydrochloric acid before precipitating the proteins with colloidal ferric hydroxide. Blood does not contain maltose. The bound sugar probably exists as a polysaccharide. If mercuric chloride is used to precipitate the proteins, no marked increase of reducing power is caused by hydrolysis. W. O. K.

Exchange of Chlorine between the Red Blood Corpuscle and the surrounding Solution. I. The Influence of Narcotics on the Exchange of Chlorine. R. SIEBECK [in part with D. HACKMACK] (*Arch. exp. Path. Pharm.*, 1922, 95, 93—103).—Urethane increases the permeability of the red blood-cells to chlorine-ions, and its action is parallel to its effect in inhibiting the oxidation processes in the cell. For example, both effects are reversible on removal of the urethane. Similar results are obtained by the use of other narcotics such as methyl, ethyl, propyl, *n*-butyl, and amyl alcohols, diethylurea, and phenylurea. W. O. K.

Coagulation of the Blood. II. Thrombin and Antithrombins. JOHN WILLIAM PICKERING and JAMES ARTHUR HEWITT (*Biochem. J.*, 1922, 16, 587—598; cf. this vol., i, 393).—The failure of the blood to coagulate after the injection of thrombin is not due to the secretion by the liver of an excess of antithrombin. The antithrombin obtained from liver is a post-mortem product. Yeast and hydrolysed edestin are also capable of yielding a similar principle which is a product resulting from the hydrolysis of pro-

tein. The addition of thrombin to blood in the state of a reversible gel causes immediate coagulation. Thrombin seems to be the accelerator rather than the initiator of coagulation. S. S. Z.

The Carbamino-reaction of the Blood-proteins and their Alleged Importance in the Transport of Carbon Dioxide by the Blood. CAMILLO AUSENDA (*Biochem. Z.*, 1922, **132**, 188—196).—From experiments on blood, serum, ascites-fluid, and pleural exudate, the author finds no evidence that Siegfried's alleged "carbamino-acids" play any part in the transport of carbon dioxide. If these fluids be saturated with carbon dioxide in the presence of milk of lime, or sodium carbonate or hydroxide and the proteins then precipitated by ammonium sulphate or obtained free from simple constituents by dialysis, there is no greater quantity of carbon dioxide fixed by the protein than in the normal physiological state of the blood. H. K.

Colloidal Equilibrium of Blood Serum. ROGER FISCHER (*Compt. rend. Soc. Biol.*, 1922, **87**, 124—126).—Experiments were carried out on serum, and on the isolated proteins from serum and from egg, in order to determine whether or not there is a physical equilibrium between the albumin and globulin in the blood, the coagulation either by alcohol or by heat being examined in the presence of a 0.2% solution of gelatin. The globulin, like the whole serum, is found to be stabilised whilst the albumin becomes less stable. The globulin acts as a stabiliser for the serum-albumin, and this relationship is found to be general. The most stable ratio (50 parts of globulin to 100 parts of albumin) closely approaches that of the two proteins in the blood.

CHEMICAL ABSTRACTS.

The Separation of the Globulins of Horse's Serum. M. VILA (*Compt. rend.*, 1922, **175**, 728—731; cf. Piettre and Vila, this vol., i, 63).—The globulins in the serum may be fractionated into three groups by addition of N/100-hydrochloric acid and subsequent treatment of the precipitate with acetone. The fraction so obtained contains globulin which is insoluble in acid under the conditions specified by the author. Another fraction separates on elimination of the added acid. The third fraction remains in solution: it has the character of serum-albumin. H. J. E.

Cholesterol Content of Blood-serum. HERMANN STRAUSS and WOLFGANG SCHUBARDT (*Zentr. inn. Med.*, 1922, **43**, 425—432; from *Chem. Zentr.*, 1922, iii, 582).—Data are given for the cholesterol content of pathological blood-sera. From a consideration of fat exchange, it would appear that necrobiotic processes play a part in the changes in cholesterol content of sera. G. W. R.

Human Mixed Saliva. I. Determination of the Hydrogen-ion Concentration of Human Mixed Saliva. II. Variations in the Hydrogen-ion Concentration. HENRY E. STARR (*J. Biol. Chem.*, 1922, **54**, 43—54, 55—64).—I. The saliva is collected under oil to prevent loss of carbon dioxide. A. portion (1 c.c.) is

diluted with freshly-boiled distilled water (9 c.c.) and the P_H estimated colorimetrically, using bromo-thymol blue (1 c.c. of a 0.01% solution) as indicator.

II. Using this method, the P_H values of 610 specimens of human mixed saliva were found to vary between 5.75 and 7.05, 86% of the specimens giving values between 6.35 and 6.80. The hydrogen-ion concentration of saliva varies directly with the alveolar carbon dioxide, increases after a meal and during exercise, and decreases as a result of voluntary deep breathing in the open air or of emotional excitement. Ingestion of large doses of sodium hydrogen carbonate decreases the salivary P_H and increases the urinary P_H .

E. S.

Metabolism of Inorganic Salts. I. The Inorganic-ion Balance of the Blood in Parathyroid Tetany. ERWIN G. GROSS and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1922, 54, 105--120).—The blood of dogs with parathyroid tetany showed a low calcium and a high potassium content; the values for other inorganic ions were approximately normal. Tetany is thus allied to a disturbance in the ratio of potassium to calcium and consequently of total univalent to total bivalent ions.

E. S.

The Metabolism of Calcium. R. ROSEMAN (*Arch. Néerland. physiol.*, 1922, 7, 358—361).—The consumption of large quantities of flesh increases the excretion of calcium. A low body content of calcium increases the readiness to hay-fever, the administration of calcium chloride acting beneficially. With increased calcium in the diet there results a retention of potassium, presumably to be explained by the antagonistic physiological action of calcium and potassium, and also an increased output of sodium.

W. O. K.

Some Induced Reactions and their Analogues in the Animal Body. N. N. MITTRA and N. R. DHAR (*Z. anorg. Chem.*, 1922, 122, 146—150).—The authors point out that many substances—proteins, carbohydrates, fats, etc.—which undergo oxidation in the animal body are under ordinary conditions stable in the presence of oxygen. The oxidation of these substances is readily induced by ferrous hydroxide, and it is argued that the iron of the blood induces the oxidation in the body. In the case of oxidation, the authors find that only easily oxidisable substances can act as negative catalysts; this is supported by several examples.

W. T.

The Gonads of *Rhizostoma Cuvieri*. FELIX HAURWITZ (*Z. physiol. Chem.*, 1922, 122, 145—159; cf. A., 1921, i, 206).—The gonads, after being freed from fat, were extracted with alcohol and with water, and in these extracts and in the residue the following substances were found on examination: potassium, sodium, magnesium, calcium, iron, chlorine, sulphate and phosphate, taurine, *o*- and *p*-cresolsulphonic acids, trimethylamine, betaine, choline, and various peptides and proteins containing alanine, tyrosine,

glutamic acid, arginine, phenylalanine, cystine, lysine, proline, and leucine. W. O. K.

Influence of the Dextrose Concentration and of the Alkalinity on Glycolysis in Vitro. P. MAURLAC and L. SERVANTIE (*Compt. rend. Soc. Biol.*, 1922, 87, 200—201).—Experiments with blood and with various organs (lung, testes) show that the amount of dextrose that is destroyed under standard experimental conditions bears a close relation to the initial dextrose content of the solution. The glycolysis is not always proportional to the quantity of sugar. The curve of the percentage loss of sugar gives the optimum point at a concentration of dextrose of about 0.3%. Similarly, the glycolysis is dependent on the reaction of the medium, a P_H of 7.8 being the optimum. This reaction corresponds with that which has also been shown to be most favourable to the consumption by the heart of sugar from the artificial circulating fluid. CHEMICAL ABSTRACTS.

The Evolution of Oxidative Enzymes. G. MARINESCO (*Compt. rend. Soc. Biol.*, 1922, 87, 31—34).—The author studied the oxydase reaction of various tissues, especially the nerve-tissue, in human embryos of different age and concludes that there is a double mechanism of respiration in the cell: (1) The iron plays the role of a catalyst and is present in the nucleus where there are no oxydases, and (2) the oxydase granules found in abundance in the cell are identified as mitochondria. CHEMICAL ABSTRACTS.

Role of Hydrogen and Hydroxyl-ion Diffusion in Nerve and Muscle Action. ELLIOT Q. ADAMS (*J. Physical Chem.*, 1922, 26, 639—649).—A theoretical paper in which calculations have been made based on the assumptions that nerve and muscle action depend on an autocatalytic conversion of dextrose or galactose into lactic acid, kept in check by diffusion, and that the significant factors in the initiation of a response are the autocatalytic reaction and the diffusion of hydrogen and hydroxyl ions. In plasma, the reaction of which is that of normal blood, $[H^+] 0.45 \times 10^{-7}$, P_H 7.35, and X_H —0.55 where X_H is the hydrogen-ion potential relative to pure water at 37°, the reaction within the excitable nerve or muscle fibre is calculated to lie between $[H^+] 0.51 \times 10^{-7}$, P_H 7.29, X_H —0.49, and $[H^+] 1.03 \times 10^{-7}$, P_H 6.99, X_H —0.19. For effective stimulation, the reaction must be acidified locally within the fibre to a critical value which depends on the concentration of enzyme (lactacidase) present in the fibre, and must be more acid than the last-named figure $[H^+] > 1.03 \times 10^{-7}$, $P_H > 6.99$, $X_H > -0.19$. It is calculated that a plasma reaction of P_H 6.92, $[H^+] 1.20 \times 10^{-7}$, X_H —0.12 will abolish the response of nerve or muscle. This is in agreement with the observation of Van Slyke that the most acid reaction during life (in deep coma) is P_H 6.95, $[H^+] 1.12 \times 10^{-7}$, X_H —0.15. J. F. S.

Production of Acetoacetic Acid from Urocanic Acid in the Surviving Liver. M. KONISHI (*Z. physiol. Chem.*, 1922, 122, 237—240).—On transfusing the liver of a dog with urocanic

acid or with glyoxalinelactic acid, a small amount of acetoacetic acid is formed; the amount is rather more than after transfusion with histidine. W. O. K.

The Proteolytic Enzymes of the Kidneys. S. G. HARDIN (*Z. physiol. Chem.*, 1922, 122, 307—317).—The kidneys of horses contain an enzyme attacking peptone with an optimum P_H of 7.8, and an enzyme attacking casein in acid solution. Preliminary treatment of the kidneys with acid increases the action of the enzymes, due apparently to the fact that the enzymes are gradually destroyed at approximate neutrality. W. O. K.

A New Constituent of the Thyroid. UBALDO SAMMARTINO (*Biochem. Z.*, 1922, 132, 293—294).—Freshly and finely divided thyroids (400 grams) were extracted with hot dilute acetic acid, and the solution concentrated and precipitated with basic lead acetate. The lead-free filtrate was concentrated and precipitated with alcohol. The filtrate from this gave potassium picrate, and then a red picrate unmelted at 300°, and a picrate, m. p. 255—295°. After removal of picric acid from the mother-liquors, addition of alcohol precipitated a crystalline substance, m. p. 225—228°, which contained calcium, nitrogen, carbon, and a large proportion of oxygen. H. K.

The Influence of the Thyroid on Creatine-Creatinine Metabolism. PAUL SCHENK (*Arch. expt. Path. Pharm.*, 1922, 95, 45—63).—In thyroidectomised rabbits, the blood creatinine is not markedly decreased, but the excretion of preformed creatinine in the urine shows a marked diminution. A marked increase then takes place on administration of thyroid extract. W. O. K.

Mechanism of the Contraction of Striated Muscle produced by Poisons. V. The Action of Specific Muscle Poisons on Lifeless Colloids. OTTO RIESSER and S. M. NEUSCHLOSZ (*Arch. expt. Path. Pharm.*, 1922, 94, 190—221).—Characteristic changes in the viscosity of a gelatin solution are produced by addition of muscle poisons such as veratrine, strophanthin, digitalin, quinine, caffeine, nicotine, and novocaine, but not by poisons (morphine, codeine, atropine, acetylcholine) which have no typical action on muscle. Where the physiological actions of the poisons are similar, as, for example, in the cases of strophanthin and digitalin, the influence on the viscosity is also similar; in other cases it is dissimilar. The physiological antagonism between veratrine and novocaine and veratrine and atropine is paralleled by an antagonistic influence on the viscosity of gelatin solutions; the mechanism of the antagonism is, however, different in the two cases. It is concluded that the action of muscle poisons is due to the changes which they produce in the colloids of the muscles. E. S.

Tension and Extensibility of Muscle during Contraction by Acids or Chemical Means. F. VERZAR, J. BOEGL, and W. SZANTY (*Biochem. Z.*, 1922, 132, 64—81).—The tension developed

in an acid solution of P_n less than 3 is less than that in normal contraction of muscle, whilst aqueous solutions of chloroform, ethyl and methyl alcohols, glycerol, aniline, and ammonia produce considerable tension. The extensibility of muscle is increased by acid over that of normal muscle and the above-named reagents diminish it. The results support von Fürth's theory of muscle contraction.

H. K.

The Replaceability of Potassium by Uranium in Cross-stripped Muscle. F. VERZÁR and W. SZÁNYI (*Biochem. Z.*, 1922, 132, 53—63).—The sartorius muscle of the frog, immersed in sodium chloride solution, exhibits fibrillary movements which are inhibited by equimolecular quantities of potassium or uranium salts. The action is reversible in both cases, but only so in the case of uranium if long contact is avoided. Emanation is without action on the fibrillary movements. If the movements be inhibited by potassium or uranium, then addition of the other restores the movements to some extent.

H. K.

The Materials Extracted from Muscles. XXI. The Organic Bases of the Flesh of Swine. I. A. SMORODINCEV (*Z. physiol. Chem.*, 1922, 123, 116—129).—Using more than 2 kilos. of pig's flesh, the following approximate figures are found for the content in organic bases: creatine, 0.228%; purines, 0.086%; carnosine, 0.289%; methylguanidine, 0.032%; carnitine, 0.032%. As compared with other animals investigated, it is particularly rich in creatine and carnosine.

W. O. K.

The Action of Digitalis, Calcium, and Barium on Strips of Heart Muscle (Löwe) and the Antagonistic Influence of Cocaine, Magnesium, and Potassium. MARTIN BRANN (*Arch. exp. Path. Pharm.*, 1922, 94, 222—234).—Contrary to Löwe's statement, digitalin produces contractions in strips of ventricle free from ganglia, an action which is antagonised by cocaine and potassium chloride. Calcium chloride, which resembles digitalin in its action, is similarly antagonised by cocaine, magnesium chloride, and potassium chloride. The two last substances, but not cocaine, also antagonise the tonic action of barium chloride.

E. S.

Potassium-Calcium Equilibrium in Animal Systems. H. ZWAARDEMAKER (*Biochem. Z.*, 1922, 132, 95—102).—A discussion of this subject with reference to replacement of potassium by uranium and thorium in Ringer's solution.

H. K.

Decarboxylation. K. SPIRO (*Arch. Néerland. physiol.*, 1922, 7, 227—233).—A general review of the place of decarboxylation in biochemical phenomena.

W. O. K.

The Non-protein Nitrogen in Goat's Milk. WILLIAM TAYLOR (*Biochem. J.*, 1922, 16, 611—612).—There was found a correlation in a lactating goat between the output of nitrogen in the urine and the percentage of non-protein nitrogen in the milk. Both seem to be determined by the amount of protein in the food.

S. & Z.

The Excretion by the Gastric Mucous Membrane and the Salivary Glands of Alkaloids Administered Subcutaneously. KARL JAKOB HUBER (*Arch. exp. Path. Pharm.*, 1922, 94, 327—351).—The literature on the excretion of alkaloids after administration to animals is reviewed. In experiments described, various alkaloids were injected subcutaneously in dogs. Atropine and eserine were excreted neither in the stomach nor in the saliva; arecoline was detected in the saliva, but not in the stomach; papaverine and veratrine, on the other hand, appeared in the stomach.

E. S.

Permeability of the Intestine to Sucrose. PIERRE WORINGER (*Compt. rend. Soc. Biol.*, 1922, 86, 1093—1095).—When either mono- or di-saccharides are ingested in quantities exceeding the assimilative capacity of the organism, the excess is eliminated through the urine. In this case the disaccharides must first undergo cleavage into two monosaccharide molecules. The disaccharide, however, also appears in the urine as such and can be demonstrated by the change in the reducing power of the urine following acid hydrolysis. In this way the author shows that, both in dogs and in babies, a fixed amount of disaccharide (on the average 1.56% and 1.58% respectively) appears in the urine and this is independent of the actual amount of sucrose fed or the body weight of the organism. This is thought to demonstrate direct permeability of the intestinal mucosa to sucrose.

CHEMICAL ABSTRACTS.

Application of the Methods of Correlation to the Study of the Urine. CHARLES POWELL WHITE (*Lancet*, 1922, [I], 202, 369—371).—An attempt to determine the manner in which the various radicles in urine are associated in solution by an examination of the correlation coefficients derived from existing series of analyses of the urine of cancerous persons. As preliminary conclusions evolved from this statistical inquiry, it is suggested that (a) sodium, potassium, and chlorine are excreted in association with the water and hence through the glomeruli; urea, uric acid, and sulphate are excreted independently of the water and therefore presumably through the tubules; phosphate, magnesium, and calcium may be excreted by both channels; (b) the association of urea with sulphuric and phosphoric acids demands further investigation; (c) uric acid may be excreted as calcium and potassium urates, but not as sodium urate; (d) potassium is excreted chiefly as chloride; (e) sodium is excreted as chloride, phosphate, and sulphate; (f) calcium and magnesium are excreted chiefly as chlorides, phosphates, and sulphates; (g) there are no indications of the excretion of alkali salts of ethereal sulphuric acids.

A. A. E.

The Relation between the True Reaction of the Urine and the Alveolar Tension of Carbon Dioxide. GUSTAV ENDRÉS (*Biochem. Z.*, 1922, 132, 220—241).—Parallel observations have been made on the P_{H_2} of the urine by a colorimetric method and the alveolar tension of carbon dioxide. After a meal, both curves

show a similar tendency, the P_H curve rising to a maximum after two or three hours and the alveolar tension of carbon dioxide rising to a maximum. The form of the curves also depends on the diet, flesh diet giving steeper curves than carbohydrate diet. It is very probable that the hydrochloric acid secretion of the stomach is largely responsible for these variations. Drugs, sleep, muscular activity, and bleeding have their effects traceable in the curves.

H. K.

Some New Observations on the Relation between the True Sugar Content of Urine and the Sugar Content of Blood. D. G. COHEN TERVAERT (*Arch. Néerland. physiol.*, 1922, 7, 352—354).—There does not seem to be any direct quantitative relation between the sugar content of the urine and that of the blood, following the consumption of quantities of dextrose. W. O. K.

Organic Acids in Urine. R. GOIFFON and F. NEPVEUX (*Compt. rend. Soc. Biol.*, 1922, 86, 1132—1133; from *Chem. Zentr.*, 1922, iv, 409).—Using the method of Van Slyke and Palmer (*A.*, 1920, i, 459), the authors found in cases of acetonuria increase in total organic acids and in β -hydroxybutyric acid in the urine. Sufficient agreement was not obtained for these acids to be regarded as the sole factor in acetonuria. The organic acid content is independent of the acidity. Sodium hydrogen carbonate renders the urine alkaline without diminution in the organic acid content.

G. W. R.

Blood in Impaired Cell Respiration. Cause of Avian Beri-beri. ALFRED FLEISCH (*Arch. exp. Path. Pharm.*, 1922, 95, 17—35).—Pigeons suffering from avian beri-beri show a decrease in the difference of the arterial and venous tensions of carbon dioxide, and also a similar decrease with regard to oxygen. A similar effect is found in pigeons suffering from cyanide poisoning. These results are taken to support Hess's view that the essential change in avian beri-beri is a decrease in the rate of cell oxidations (cf. this vol., i, 399).

W. O. K.

Diabetes, β -Hydroxybutyric Acid, and Lævulose. A. DESGREZ, H. BIERRY, and F. RATHERY (*Compt. rend.*, 1922, 175, 536—539).—Different sugars are not interchangeable in a diabetic ration; their molecular structures affect to a considerable extent the results of assimilation. The authors consider that it is necessary to deal with the specific results to be obtained from each sugar. The ingestion of lævulose furnishes a remedy for certain irregularities of metabolism; in cases of diabetes, it provides a means of preventing or reducing the elimination of β -hydroxybutyric acid. When the carbohydrate tolerance of a diabetic patient has been determined, it is sufficient to administer lævulose associated with phosphates and with vitamin-B to the ascertained limit.

H. J. E.

Examination of the Pentose in a New Case of Pentosuria. A. N. WRZESNEVSKI (*Biochem. Z.*, 1922, 132, 135—137).—The pentose excreted in a case of pentosuria in a female was identified

as *r*-arabinose, by means of its diphenylhydrazone and its phenyl-osazone. H. K.

The Chemical Nature of Toxins and Antitoxins. E. SALKOWSKI (*Biochem. Z.*, 1922, 132, 84—88).—The author recalls some unpublished experiments made by himself in 1896 on the preparation of diphtheria antitoxin free from protein. The diphtheria antitoxin serum was saturated with sodium chloride, treated with two volumes of saturated sodium chloride solution, and trichloroacetic acid added so long as there was a precipitate. The protein precipitate carried the antitoxin down with it. The product is filtered off and triturated with water which dissolves the antitoxin. The solution is free or practically so from protein. The same procedure has been employed by Blumenthal (*Z. klin. Med.*, 1896, 30) for the preparation of protein-free toxin from the spinal marrow of a case of tetanus. H. K.

Influence of the Sodium-ion in the Production of Tetany. FREDERICK F. TISDALL (*J. Biol. Chem.*, 1922, 54, 35—41).—Disodium phosphate, injected intravenously into four dogs, produced a condition resembling active tetany in one case and an incipient tetany in the remainder; phosphoric acid, on the other hand, produced no marked effect. Analyses of the inorganic constituents of the blood indicate that the important factor in the production of tetany is a disturbance of the sodium-calcium ratio. In the case of gastric tetany, however, increase in the bicarbonate ion is apparently responsible. E. S.

The Behaviour of Phenyl-lactic Acid in the Animal Organism. I. Y. KOTAKE and Y. MORI (*Z. physiol. Chem.*, 1922, 122, 176—185).—After *dl*-phenyl-lactic acid has been administered to dogs, rabbits, or monkeys, their urine contains the *d*-acid, along with the inactive isomeride. With man, on the other hand, the *l*-acid is present in excess in the urine after administering *dl*-phenyl-lactic acid. W. O. K.

The Behaviour of Phenyl-lactic Acid in the Animal Organism. II. Y. MORI (*Z. physiol. Chem.*, 1922, 122, 186—190).—The resolution of phenyl-lactic acid by means of the strychnine salt is described, and the following rotations were found: *d*-phenyl-lactic acid, m. p. 124°, $[\alpha]_D^{20} +20.92^\circ$; *l*-phenyl-lactic acid, m. p. 124°, $[\alpha]_D^{20} -19.86^\circ$. After *d*-phenyl-lactic acid is administered to man, phenylpyruvic acid is found in the urine along with unchanged material. If the *l*-acid be administered, smaller amounts of phenylpyruvic acid are found. With dogs, only very small amounts of phenylpyruvic acid are formed from either acid. W. O. K.

The Behaviour of Phenylpyruvic Acid in the Animal Organism. Y. KOTAKE and Y. MORI (*Z. physiol. Chem.*, 1922, 122, 191—194).—Both in men and in dogs, phenylpyruvic acid is reduced to *l*-phenyl-lactic acid, this being found in the urine. W. O. K.

The Behaviour of Phenylalanine in the Animal Organism. Y. KOTAKE, Y. MASAI, and Y. MORI (*Z. physiol. Chem.*, 1922, 122, 195—200).—After the administration of *dl*-phenylalanine to rabbits, phenylpyruvic acid, hydroxyphenylpyruvic acid, and *l*-hydroxyphenyl-lactic acid, along with *d*-phenylalanine, are found in the urine. *d*-, *l*-, and *dl*-Phenylalanines can all be oxidised by the animal organism to phenylpyruvic acid.

W. O. K.

The Excretion of Hydroxyphenyl-lactic Acid after Administration of Tyrosine to Rabbits. Y. KOTAKE and M. OKAGAWA (*Z. physiol. Chem.*, 1922, 122, 201—205).—Only very small quantities of hydroxyphenyl-lactic acid are found along with much larger amounts of hydroxyphenylpyruvic acid in the urine of rabbits after administration of *l*- or *dl*-tyrosine. No evidence could be obtained that hydroxyphenyl-lactic acid can be converted into hydroxyphenylpyruvic acid.

W. O. K.

The Asymmetrical Reduction of Ketonic Acids to the Corresponding Alcohols in Organs. Y. MORI and T. KANAI (*Z. physiol. Chem.*, 1922, 122, 206—210).—Phenylpyruvic acid and hydroxyphenylpyruvic acid are reduced by the liver, kidney, and spleen to *l*-phenyl-lactic acid and *l*-hydroxyphenyl-lactic acid.

W. O. K.

The Behaviour of Amino-acids in Vitrally Stained Animals. I and II. Y. KOTAKE, Y. MASAI, and Y. MORI (*Z. physiol. Chem.*, 1922, 122, 211—219, 220—224).—If phenylalanine or tyrosine be administered to a rabbit which has been vitally stained by the injection of an alkaline carmine solution, there is less phenylpyruvic acid or hydroxyphenylpyruvic acid in the urine than in the absence of the staining. Vital staining, therefore, appears to inhibit the oxidative deamination of amino-acids. It also inhibits the oxidation of phenylalanine to tyrosine as shown by transfusion experiments on the liver after death. On the other hand, the production of acetoacetic acid from phenylalanine is not interfered with.

W. O. K.

Comparative Researches on the Production of Acetoacetic Acid from *d*- and *l*-Phenyl-lactic Acids and from *d*- and *l*-Hydroxyphenyl-lactic Acid in the Surviving Liver. Y. MORI (*Z. physiol. Chem.*, 1922, 122, 225—229).—*dl*-Hydroxyphenyl-lactic acid has been resolved through its morphine salt, and the following constants have been found: *d*-hydroxyphenyl-lactic acid, $[\alpha]_D +18.87^\circ$; *l*-hydroxyphenyl-lactic acid, $[\alpha]_D -18.92^\circ$. On transfusion through the liver of a dog, both forms of phenyl-lactic acid give rise to small amounts of acetoacetic acid, the *l*-form being the more effective. *l*-Hydroxyphenyl-lactic acid likewise yielded a small amount of acetoacetic acid, the *d*-form, none at all.

W. O. K.

The Production of Urocanic Acid from Histidine in the Dog. Y. KOTAKE and M. KONISHI (*Z. physiol. Chem.*, 1922, 122, 230—236).—Urocanic acid can be isolated from the urine of

a dog after the administration of histidine either by the mouth or by subcutaneous injection. No urocanic acid was found after the administration of glyoxaline-lactic acid. W. O. K.

The Deaminating of Tyrosine in the Animal Organism. Y. KOTAKE, Z. MATSUOKA, and M. OKAGAWA (*Z. physiol. Chem.*, 1922, 122, 166—175).—In the urine of a rabbit to which *L*-tyrosine had been administered, *L*-hydroxyphenyl-lactic acid and hydroxy-phenylpyruvic acid were found, and also a small amount of *DL*-hydroxyphenyl-lactic acid; whilst, after *DL*-tyrosine had been given, hydroxyphenylpyruvic acid, *L*-phenyl-lactic acid, and *D*-tyrosine were found. Phenol is also present. W. O. K.

The Deamination of Amino-acids and the Reversible Transformations of the Products so arising in the Animal Organism. Y. KOTAKE (*Z. physiol. Chem.*, 1922, 122, 241—244).—A summary of the work of the author and his collaborators on this subject (cf. preceding abstracts). W. O. K.

Formaldehyde in the Urine after Administration of Hexamethylenetetramine. KURT VOIT (*Arch. exp. Path. Pharm.*, 1922, 95, 124—128).—Formaldehyde may be detected in the urine after the administration of hexamethylenetetramine, but its presence has not been established in blood or other body fluids. W. O. K.

Physiological Researches on Vitamin-B and Water-soluble Biocatalysts. G. JONSON BLOHM, C. G. SANTESSON, and H. VON EULER (*Arkiv Kem. Min. Geol.*, 1922, 8, No. 13, 1—27).—Various preparations from yeast and malt which accelerate the growth of yeast lower the blood-pressure if injected into rabbits, reduce the pulse-rate, and also affect the breathing. They are, however, only very slightly less active as biocatalysts after inactivation by heating, except in the case of particularly pure preparations where the difference is more marked. W. O. K.

Chloroform in the Blood after Death. C. S. GIBSON and P. P. LAIDLAW (*Guy's Hospital Reports*, 1922, July, 359—366).—Estimations of the chloroform in the heart blood of rabbits killed by an overdose of chloroform show a larger amount a few days after death than at death, an increase apparently due principally to the passage of liquid from the vascular system after death. W. O. K.

Chemistry of Vegetable Physiology and Agriculture.

The Mechanism of the Reversal in Reaction of a Medium which takes place during growth of *Bacillus diphtherie*. CHARLES GEORGE LEWIS WOLF (*Biochem. J.*, 1922, 16, 541—547).—The reversal of reaction from acidity to alkalinity in carbohydrate-free media caused by the growth of *Bacillus diphtherie* is due

partly to the production of volatile acids. These acids are converted into carbonates when the medium becomes more alkaline. Organic acids such as malic and succinic acids are also utilised to produce carboxates. Formic acid is not formed as an intermediate product.

S. S. Z.

Decomposition of Citric Acid of Cow's Milk by some Bacteria. HEINRICH KICKINGER (*Biochem. Z.*, 1922, 132, 210—219).—The citric acid content of milk is unchanged when the milk is boiled or pasteurised, but falls off on long keeping. In fractionally sterilised milk, the citric acid content falls off during the first day but remains constant after the third sterilisation. This is not due to lactic acid forming bacteria but to peptonising bacteria (*Bacillus subtilis*, *Proteus vulgaris*).

H. K.

Influence of Radioactive Substances on Acetic Fermentation. LABORDE, JALOUSTRE, and M. LEULIER (*Bull. Soc. Chim. Biol.*, 1922, 4, 415—418).—The acetic fermentation of wine is at first accelerated and later retarded by the addition of mesothorium in amounts not greater than that equivalent to one micro-gram of radium bromide per 100 c.c. Concentrations of thorium-X greater than this completely stop the fermentation.

E. S.

Action of Ultra-violet Rays on *Saccharomyces cerevisiae*. ROMOLO DE FAZI and REMO DE FAZI (*Giorn. Chim. Ind. Appl.*, 1922, 4, 463—464).—The results previously obtained (A., 1916, i, 236) have been confirmed in a large scale experiment on a brewery wort.

T. H. P.

Activators of Fermentation. ERNST LINDBERG (*Biochem. Z.*, 1922, 132, 110—134).—The accelerating influence of yeast water, yeast co-enzyme, and milk has been determined on washed and unwashed dried yeast; and also the influence of abietic acid, amyria, and cholesterol. The former group accelerate the fermentation but the latter are without action. Pyruvic acid is fermented more rapidly than dextrose but lactic acid was practically untouched.

H. K.

Behaviour of some Amino-acids towards Oxygenated Yeast. FRITZ LIEBEN (*Biochem. Z.*, 1922, 132, 180—187).—Unlike lactic acid, amino-acids are not quickly destroyed by oxygenation of their solution in presence of yeast-cells.

H. K.

Further Experiments on the Destruction of Lactic Acid by Yeast. OTTO FÜRTH and FRITZ LIEBEN (*Biochem. Z.*, 1922, 132, 165—179; cf. this vol., i, 502).—The disappearance of lactic acid observed on shaking yeast suspensions in a current of oxygen could not be attributed to the formation of simple derivatives such as acetaldehyde or β -hydroxybutyric acid, etc.; half of the carbon of the lost lactic acid does, however, appear as carbon dioxide, the other half possibly being utilised in the building up of tissue.

The Chemical Composition and the Bouquet of Wines. PHILIPPE MALVEZIN (*Ann. Chim. Analyt.*, 1922, 4, 298—301).—The fact of a substance being capable of exciting the sense of smell is attributable to the presence of certain chemical groups in its molecule, which by analogy to chromophores are termed osmophores. Thus the groups -CHO , -CN , and -NO_2 are osmophores which when attached to the benzene nucleus give rise to the odour of almonds. Similarly, the traces of ethers, esters, and other odorous substances which are slowly formed in wines on keeping exert a marked effect on the odour of the wine, and owing to the extreme sensitiveness of such organoleptic tests, it is possible to detect the presence of combinations of osmophores, as, for example, -CO- and -CH_3 in ethyl acetate, an important constituent of matured wines, when ordinary chemical tests would fail.

G. F. M.

The Influence of the Constitution of Nutritive Media on the Composition of *Aspergillus niger*. ÉMILE F. TERROINE, R. WURMSER, and J. MONTANÉ (*Compt. rend.*, 1922, 175, 541—544).—The nitrogen content of *Aspergillus niger* decreases during the course of development, does not vary with concentration of nitrogenous food, and decreases considerably in media rich in sugar with the exception of young cultures which increase in nitrogen content with increasing concentration of available carbohydrate. The substitution of urea or sodium nitrate for ammonium sulphate in the nutritive medium scarcely modifies the quantity, that of peptone or guanidine considerably lowers it, whilst changes in the sugar exert little influence except for the lower values obtained in presence of galactose. When nitrogen is absent from the culture medium, the nitrogen content is considerably lower.

H. J. E.

Fermentation of Pentoses by Moulds. W. H. PETERSON, E. B. FRED, and E. G. SCHMIDT (*J. Biol. Chem.*, 1922, 54, 19—34).—Out of twenty-five species of moulds investigated, sixteen were found rapidly to ferment both xylose and arabinose; the destruction of the pentoses was, however, somewhat less rapid than that of dextrose. *Aspergillus niger* and other species of *Aspergillus* were especially active in fermenting the pentoses. *Penicillium glaucum* was also active, but with other *Penicillia* the fermentation proceeded slowly. In agreement with results obtained by others, it was found that more than 90% of the carbon of the pentose consumed could be accounted for as carbon dioxide and mycelium. No volatile acid or alcohol was produced, but a small quantity of a non-volatile acid appeared to be formed.

E. S.

Urea and Urease in Fungi. A. GORIS and P. COSTY (*Compt. rend.*, 1922, 175, 530—541; cf. Goris and Mascré, A., 1909, ii, 175).—The results of a considerable number of experiments show that urease is present in almost all the higher fungi. In those species

in which the ferment is absent or is present only in very small quantity, urea is found in variable percentage in the mycelium.

H. J. E.

The Relation between the Colloidal State and the Physiological Functions of Protoplasm. RENÉ WURMSER and RAYMOND JACQUOT (*Compt. rend.*, 1922, 175, 782—784).—Seaweed, when heated for two minutes in sea-water, undergoes a greater reduction in its assimilative than in its respiratory function, the excess of disengaged oxygen over absorbed oxygen decreasing and eventually being reversed with rise of temperature. The respiration effect was also determined in darkness, thus excluding assimilation, and was found to be small in comparison with the latter, although its rate of diminution with rise of temperature is considerably less.

H. J. E.

The Effect of the Reaction of a Nutritive Solution on Germination and the First Stages of Plant Growth. RALPH M. HIXON (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, 4, No. 9, 1—28).—To study the effect of hydrogen-ion concentration on the germination of seeds and the early growth of plants, experiments were made with peas, cereals, and carrots. The nutritive solution used was Tollen's solution, of which the P_H was varied as required by the addition of hydrochloric acid or sodium hydroxide; other experiments were made with tap water and with sterilised agar. Germination took place over the wide range of P_H 4 to 7.6 with only slight variation at the two extremes, but in the middle part of the range there was a point where the rate of germination was a minimum. This point was at P_H 5.0 for peas, P_H 6.0 for maize, wheat, and oats, and P_H 5.5 for carrots. On the other hand, the root growth of carrots was a maximum at his critical point at the end of the tenth day. The author is inclined to interpret the critical point as that of greatest efficiency and the point of normal growth. It is difficult, however, to define a standard for normal growth. There is always a tendency, when a plant is growing in a solution with a P_H value lying towards one extreme, for the plant to modify this value towards one lying between P_H 5.0 and 6.8. These and other observations by different authors indicate an ionic equilibrium between the roots of the plant and the salts of the solution. The greater rate of germination of seeds in solutions with P_H values lying on either side of the critical value may be due to the stimulating effect, in small concentrations, of the two toxic ions H^+ and OH^- .

E. H. R.

Some Relations of Arsenic to Plant Growth. I. JOHN TEWART (*Soil Sci.*, 1922, 14, 111—118).—The solubility of lead arsenate in solutions of salts, comparable to those existing in the soil solution was determined. In water, the solubility was three parts per million. This figure was scarcely affected by the presence of neutral sulphates and nitrates but was markedly increased by acid salts and salts hydrolysing in solution to give an alkaline reaction. The solubility of lead arsenate in soil is roughly pro-

portional to the amount of soluble salts in the soil, with the exception of alkali soils where the figure is lower than would be expected. The presence of carbonate, hydrogen carbonate, and potassium ions appears in most cases to facilitate the solution of lead arsenate.

A. G. P.

Some Relations of Arsenic to Plant Growth. II. JOHN STEWART and EDWIN S. SMITH (*Soil Sci.*, 1922, 14, 119—126).—Crops were grown in soil to which varying amounts of disodium arsenate were added. Distinct evidence of stimulation in low concentrations was observed, although no decisive information could be obtained from the dry weights of crops obtained. Higher concentrations of arsenate proved injurious. It is suggested that the accumulation in the soil of arsenates from sprays may be beneficial, since the solubility of lead arsenate in the soil solution is sufficiently small to prevent the concentration of arsenic reaching the toxic dose.

A. G. P.

Hippuric Acid and Urea as Nutrient Materials for Plants TH. BOKORNY (*Biochem. Z.*, 1922, 132, 197—209).—In higher strengths than 0.09%, hippuric acid is toxic to plant-cells, urea at 1% being harmless.

H. K.

The Influence of Sucrose on the Greening of Etiolated Cotyledons at Various Stages of Germination. (FRL.) S. MANSKY (*Biochem. Z.*, 1922, 132, 18—25).—The etiolated embryos or shoots of the pumpkin were grown in the dark and then exposed to sucrose solutions of different strengths and at different periods of growth, in sunlight. There is a minimum concentration of sucrose which favours chlorophyll formation, an optimum and a maximum concentration, and each of these depends on the age of the embryo.

H. K.

What Becomes of Carbohydrates when the Leaves of Trees Die? RAOUL COMBES and (MLLÉ) DENISE KOHLER (*Compt. rend.*, 1922, 175, 590—592).—When the leaves turn yellow and die of the trees the amount of soluble carbohydrates decreases by about one-half during the change. Leaves which have been plucked and subsequently undergo the change of colour also diminish in carbohydrate content, but only by one-third. In both cases the insoluble easily hydrolysed carbohydrates increase in quantity; this is due to a transformation of the less easily hydrolysed polysaccharides into those more easily hydrolysed. These conclusions are drawn from a study of the leaves of *Fagus sylvatica* and *Esculus hippocastanum*, both of which species give analogous results.

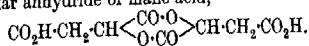
H. J. E.

Changes which Occur in the Pectic Constituents of Store Fruit. MARJORIE HARRIOTTE CARRÉ (*Biochem. J.*, 1922, 16, 704—712).—Pectin reaches a maximum during the process of ripening and then gradually falls as the fruit (apple) becomes over-ripe. The date of picking of the fruit has no effect on the development of the pectin in either cold or ordinary store. Protopectin—the

recursor of soluble pectin—can be estimated by hydrolysing the residue with *N/20*-hydrochloric acid after the soluble pectin has been extracted and utilising the calcium pectate method. Preliminary work suggests the existence of a definite relationship between the quantities of soluble pectin and protopectin constituents and that the production of soluble pectin is due to enzyme action. There is a possibility of the existence of a third soluble pectin.

S. S. Z.

Chemical Constituents of Green Plants. XXI. The Non-existence of Crassulaceæ Malic Acid. HARTWIG FRANZEN and RUDOLF OSTERTAG (*Z. physiol. Chem.*, 1922, 122, 263—297).—It appears that the third optically active form of malic acid, said to exist in *Bryophyllum*, *Crassula arborescens*, *Echeveria secunda glauca*, and other plants, does not really exist. A review of the literature suggests that it is really an impure form of ordinary malic acid, and an investigation on the acids of *Echeveria* has shown that the impurity which has been responsible for the erroneous conclusion is a bimolecular anhydride of malic acid,



The presence of this has been shown by using the ester-hydrazone method previously employed. Besides this anhydride, and much malic acid, the presence of traces of succinic acid and possibly of citric acid has been demonstrated by the same method. W. O. K.

Carrageen (*Chondrus crispus*). III. The Constitution of the Cell-wall. BARBARA RUSSELL-WELLS (*Biochem. J.*, 1922, 16, 578—586).—The chemistry of the hot and cold extracts of carrageen as prepared by Haas and Hill and by Haas (A., 1921, i, 19) was studied. Both extracts contain pentose radicles and calcium and ammonium ethereal sulphates. The ash also contains calcium, magnesium, sodium, potassium, and traces of iron. Pectic radicles are absent from both extracts. The cold extract contains a hydrolysable organic substance. On oxidation the cold and hot extracts yield mucic, oxalic, and tartaric acids—more mucic but less oxalic acid is derived from the cold than from the hot extract. The extracted residue of carrageen contains cellulose. There are indications that *Ceramium rubrum* also contains ethereal sulphates.

S. S. Z.

Botanico-chemical Notes. EDMUND O. VON LIEPMANN (*Ber.*, 22, 55, [B], 3038—3041).—During an exceptionally warm summer drops of nectar fell from the garden foxglove which solidified readily and contained large quantities of sucrose. Trehalose has been isolated from a sample of wild oats grown near Kissingen.

An exudation from the stems of a quince tree which had been damaged by smoke and was nearly dead consisted of a viscous, white gum which was very rapidly and almost completely hydrolysed by dilute acid with production of *r*-galactose.

Malic, citric, tartaric, and succinic acid have been isolated from the berries of the mountain ash; the nature and relative amounts of the acids appear to depend on the variety of berry and the degree of ripeness. H. W.

The Relation between Anthocyanin and Oxydases. MARCEL MIRANDE (*Compt. rend.*, 1922, 175, 595—597).—The development of colouring matter in scales from bulbs of *Lilium candidum* and *L. martagon* on exposure to light depends on an oxidising action. The presence of an oxydase in the scale is shown, but it is confined to that portion in which the anthocyanin is formed or which is capable of formation of anthocyanin. H. J. E.

The Relation between Tissue-acidity and the Presence of Anthocyanin in the Scales of Lily Bulbs exposed to Light. MARCEL MIRANDE (*Compt. rend.*, 1922, 175, 711—713; cf. this vol., i, 1100, and preceding abstract).—Scales from bulbs of *Lilium candidum* and *L. martagon* when detached and exposed to light undergo an increase in acid content which is due partly to the fracture and partly to the acidification which is correlated with pigmentation. The author has shown that an oxydase is present but that its distribution is limited to those cells in which the pigment is formed, whilst acidification occurs at all points. If the oxydase is a factor in the acidification which accompanies pigmentation, this is clearly differentiated from the general development of acid; if not, its only function appears to be the part played in anthocyanin development. The conclusion is drawn that this work confirms the author's statement that oxidation is a factor in anthocyanin synthesis. H. J. E.

The Transformation of a Chromogen of Yellow Flowers of *Medicago falcata* under the Action of an Oxydase. ST. JONESCO (*Compt. rend.*, 1922, 175, 592—595).—An alcoholic extract of the yellow flowers of *M. falcata* gave a clear liquid of an intense yellow colour, and a series of tests showed that the pigment was of the flavone type. Reduction of the pigment by nascent hydrogen gave a colourless solution, but the action of the oxydase obtained from *Russula delica* resulted in the production of a substance of the same colour as the violet flowers of *M. falcata*, which responded to tests in a manner characteristic of anthocyanins. Similar results are obtained by oxidation of the yellow pigment with hydrogen peroxide and the author concludes that oxidation of the chromogen leads to its transformation into an anthocyanin pigment. H. J. E.

The Phytosterols of Ragweed Pollen. FREDERICK W. HEYL (*J. Amer. Chem. Soc.*, 1922, 44, 2283—2286).—From the unsaponifiable fraction of the ether extract of the pollen of ragweed, *Ambrosia artemisiifolia*, L., the author has isolated a new phytosterol, *ambrosterol*, $C_{27}H_{46}O$, m. p. 147—149°, giving an acetate, m. p. 112—113°. In addition, this fraction contains a phytosterol, $C_{27}H_{46}O$, m. p. 147.5—148°, and considerable amounts of a more highly

oxygenated substance, probably an oxyphytosterol. Appreciable quantities of the higher homologues of the methyl alcohol series, of which cetyl and octadecyl alcohols were identified, and traces of a hydrocarbon were also found. W. G.

The Presence of Aucubin and Sucrose in Seeds of *Rhinanthus Crista-Galli*. L. MARC BRIDEL and (Mlle) MARIE BRAECKE (*Compt. rend.*, 1922, 175, 532—534; cf. A., 1921, i, 340).—Aucubin and sucrose were obtained in pure crystalline condition from the seed. H. J. E.

Nitrogenous Metabolism of Higher Plants. III. The Effect of Low-temperature Drying on the Distribution of Nitrogen in the Leaves of the Runner Bean. ALBERT CHARLES CHIBNALL (*Biochem. J.*, 1922, 16, 599—607).—On drying the leaves of the runner bean at a low temperature, some of the protein is autolysed with the production of water-soluble nitrogenous products which chiefly consist of ammonium salts, asparagine, and amino-acids. The reduced protein is, however, not appreciably changed in character. The dried leaves contain enzymes which are activated by water. The presence is indicated of an asparaginase which is activated by the addition of water and under the specified conditions manifested marked synthetic activity. S. S. Z.

Nitrogenous Metabolism of the Higher Plants. IV. Distribution of Nitrogen in the Dead Leaves of the Runner Bean. ALBERT CHARLES CHIBNALL (*Biochem. J.*, 1922, 16, 608—610).—For comparison with the seasonal variations previously described (this vol., i, 908), the nitrogen content of, and its distribution in, the dead leaf of the runner bean killed by a frost in the twenty-fourth week of its life is given. S. S. Z.

Application of Bourquelot's Biochemical Method to the Investigation of Sugars and Glucosides in some of the *Scrophulariaceæ*. (Mlle) MARIE BRAECKE (*Bull. Soc. Chim. Biol.*, 1922, 4, 407—414; cf. A., 1915, i, 631).—Nine plants were investigated and all were found to contain sugars hydrolysable by invertase and a glucoside hydrolysable by emulsin. In the cases of *Pentstemon hybridus*, *Collinsia bicolor*, Benth., *Pentstemon barbatus*, Roth., and *Freylinia cestoides*, Colla, the glucoside appears to be identical with aucubin (cf. this vol., i, 209), although in the three last plants other principles decomposable by emulsin are probably also present. E. S.

The Presence of the Glucoside of an Essential Oil in the Leafy Stems and Roots of *Sedum telephium*, Linn. MARC BRIDEL (*J. Pharm. Chim.*, 1922, [vii], 26, 289—298).—Bourquelot's biochemical method reveals the presence in the leafy stems and roots of *Sedum telephium*, a glabrous plant growing in the Vosges and elsewhere in France, a glucosidal principle giving on hydrolysis by emulsin an aromatic substance having an odour of roses. So far the glucoside has only been obtained in an amorphous condition. It is soluble in water, alcohol, acetone, or chloroform.

Its aqueous solution reduces Fehling's solution, 1 gram being equivalent to 0.103 gram of dextrose. It has $[\alpha]_D -28.57^\circ$. On hydrolysis with sulphuric acid, an aromatic substance having an odour reminiscent of eucalyptol or terpineol is produced. The different substances produced by the action of emulsin and sulphuric acid, respectively, might indicate that the fermentation product is a substance related to geraniol, which, as is known, gives terpene derivatives by the action of sulphuric acid. The reducing sugar was identified as dextrose. G. F. M.

Carbon Monoxide in Tobacco Smoke. HENRY E. ARMSTRONG and E. V. EVANS (*Brit. Med. J.*, 1922, (I), 992—993).—Hydrogen sulphide and carbon monoxide are present in tobacco smoke in minute amounts. The carbon monoxide was estimated in a Bone and Wheeler apparatus, or by Gautier's method, and found to vary with the rate of smoking, being the greater the more rapidly air is artificially drawn through the glowing tobacco, the length and temperature of the glowing portion being thereby increased. Cigarettes, smoked normally, yield a smoke containing 0.6—0.88% of carbon monoxide, pipes from 0.7—1.14%, and cigars from 6—8% (when smoked quickly). As regards cigars, the results are little affected by make or quality, closeness of packing and rate of smoking being the determining factors. A. A. E.

Differences Effected in the Protein Content of Grain by Applications of Nitrogen made at Different Growing Periods of the Plant. W. F. GERICKE (*Soil Sci.*, 1922, 14, 103—109).—Pot cultures of various cereals were fertilised with sodium nitrate periodically during the first three to four months after sowing. In general, the later the application of nitrogen was made the higher became the protein content of the matured grain. The relative variations of protein content produced, depended on the length of the normal growing period of the plant. Thus no differences were produced by fertilisation during the dormant periods of growth of winter wheat and, to a lesser extent, of rye. The hardness of the wheat grains followed the increased protein content; from a soft seed wheat the whole range from a typically soft to a typically hard grain could be produced according to the period at which nitrates were added. The size of the grains varied but little. A. G. P.

Biochemistry of Phosphorus. F. ROGOZINSKI (*Bull. Acad. Sci., Cracovie*, 1915, [B], No. 5, 87—98).—In the milling by-products of the cereals, 16—35% of the phosphate is present in an insoluble form, whilst in the residues from oil-bearing seeds the corresponding figure is 50—82%. Most of the soluble phosphate of the maize kernel, including all the phytin phosphate, is present in the germ. In the case of sprouted malt, the inorganic phosphate is found to increase at the expense of the phosphorus in the proteins and the phytin. The phytin phosphate appears to be stored in the outer

portion of the wheat kernel. Rye bran is comparatively poor in phytin phosphate but rich in inorganic phosphate. For the preparation of phytic acid, wheat bran, rice fodder, and rape press cake are the only considerable sources. Coconut press cake has a high content of phytin, and a low content of phosphate, whilst the reverse is true for palm nut press cake. It was observed in the case of the wheat kernel that all the inorganic phosphate is soluble in water, and is present as potassium phosphate. This appears to be the case also in other seeds. CHEMICAL ABSTRACTS.

Absorption (by Soil) of Ammonium Ions from Solutions of Ammonium Salts and the Effect of Electrolytes thereon.

B. AARNIO (*Z. Pflanz. Ding.*, 1922, [A], 1, 320—325).—The absorption by soil of ammonium ions from solutions varies according to the ammonium salt used for the experiment, being approximately the same for ammonium chloride and ammonium sulphate, but greater for ammonium hydrogen phosphate. The effect of the addition of electrolytes on absorption from ammonium sulphate and ammonium hydrogen phosphate solutions was also studied. In most cases, absorption is decreased; hydroxyl ions, however, cause increase in absorption. It is held that absorption is influenced according to the effect of the substances present on the degree of dispersion of the absorbent. Electrolytes which flocculate soil decrease absorption, whilst, where a dispersing effect is exerted, absorption is increased. Soil consists both of positively and negatively charged particles and anions are absorbed to some extent as well as kations.

G. W. R.

Some Investigations on the Electrical Method of Soil Moisture Estimation. THOMAS DEIGHTON (*J. Agric. Sci.*, 1922, 12, 207—230).—The method examined consists of measuring the resistance between carbon electrodes pressed into the soil to a measured depth.

It is shown that the resistance measured is the mean resistance of a volume of soil rather larger than a sphere of which the two electrodes are the poles. The limitations of the method are discussed, and a mathematical investigation of the path of the current in the soil agrees well with experimental data.

From a consideration of a number of moisture-resistance curves, it is concluded that with moisture contents greater than 10%, the resistance varies inversely with the square of the moisture content. With less than 10% of moisture, one or more irregularities appear in the curves, depending, it would seem, on the physical conditions of the soil colloids. The possibility of determining, by this method, the depth of water tables in arid lands is indicated.

A. G. P.

Origin of Soil Colloids. NEIL E. GORDON (*Science*, 1922, 55, 676—677).—The author disagrees with Whitney's theory (this vol., i, 708) regarding the mode of formation of soil colloids, preferring to regard the process as being based largely on chemical

ABSTRACTS OF CHEMICAL PAPERS.

regions. Many soil particles are hydrated silicates containing varying amounts of aluminium, iron, silicon, sodium, potassium, calcium, magnesium, and other elements in smaller quantities; they are surrounded by an aqueous film, the salts in the outer layer being subjected to constant hydrolysis. The hydrolytic products of the soluble compounds are partly dissolved by the film, and partly adsorbed by the insoluble products of the iron and aluminium salts which form a gel casing. Percolating rain-water removes part of the soluble salts, thus destroying the salt equilibrium between the water film and the gel, and releasing some of the soluble adsorbed salt to the water film, with eventual peptisation of the gel. The latter, in the course of percolation, may again be coagulated, whilst the soil particle is again exposed to hydrolytic action. There is experimental support for this view of the origin of soil colloids.

A. A. E.

Absorption of Water by Soil Colloids. W. O. ROBINSON (*J. Physical Chem.*, 1922, 26, 647—653).—Samples of colloidal matter extracted from thirty-four soils, which differed in texture, origin, mode of formation and chemical composition, showed a relatively constant absorption of water. The soils examined included loam, clay loam, silt loam, sandy loam soils, and subsoils. The extreme absorptions were 0.240 gram and 0.348 gram of water per gram of colloid and the mean value was 0.298. It is suggested that the colloidal matter in a soil might be fairly closely estimated by determining under certain conditions the water absorption of the soil and dividing the result by the average factor 0.298.

J. F. S.

Occurrence of Sulphate Reduction in the Deeper Layers of the Earth. C. A. H. VON WOLZOGEN KÜHR (*Proc. K. Acad. Wetensch. Amsterdam*, 1922, 25, 188—198).—A number of samples of soil (peat, clay, and sand) taken from nine new wells in the Amsterdam district have been examined for the presence of the sulphate reducing organism *Microspira desulfuricans* by placing small portions in a solution containing 100 tap-water, 0.5 sodium lactate, 0.1 asparagine, 0.5 hydrated magnesium sulphate, and 0.001 hydrated ferrous sulphate at 25°. In every case, after two to twenty days the reduction of the sulphate was evident by the formation of ferrous sulphide. Consequently the grey colour of the sand and the blue to bluish-black colour of the clay point to the sulphate reduction occurring at depths from 10 metres to 34.50 metres. The bacteria have been isolated and counted and shown to be facultative anaerobic organisms. The transformation of sulphate into ferrous sulphide by *Microspira desulfuricans* explains the partial or total absence of sulphuric acid from deep dune water.

J. F. S.

